

CIII.—*The Action of Aluminium Chloride on Naphthalene.*

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Preparation and Identification of $\beta\beta$ -Dinaphthyl.

DURING the course of a series of investigations on nickel carbonyl, Dewar and Jones (Trans., 1904, **85**, 212) observed that nickel carbonyl and naphthalene in presence of aluminium chloride gave a small yield of a hydrocarbon of which the melting point, solubility, and analyses corresponded with those of a compound prepared by Bischoff (Ber., 1890, **23**, 1905) by the action of methyl chloride on a mixture of naphthalene and aluminium chloride. Bischoff had proposed for this hydrocarbon the formula $C_{16}H_{12}$ and had represented it as :



Dewar and Jones further stated that nickel carbonyl acting on benzene and aluminium bromide gave some of the above compound, whilst with benzene and aluminium chloride the products were benzaldehyde and anthracene with no trace of Bischoff's hydrocarbon.

As it seemed of some interest to investigate the above apparent difference in the specific influence of the two aluminium salts on the products of the reaction, it was with this object primarily that, at the suggestion of Mr. H. O. Jones, the work about to be described was undertaken.

The first point requiring explanation was whether the substitution of aluminium bromide for aluminium chloride in a Friedel and Crafts' reaction always leads to a difference in the products of the reaction, and if not, whether, as in the above case, it does so only when acting conjointly with nickel carbonyl. It seemed as if an explanation of all the different methods of formation of the hydrocarbon $C_{16}H_{12}$ should incidentally also furnish the answer to the above question, an anticipation that has been realised.

I. The Action of Nickel Carbonyl on Benzene in the presence of Aluminium Bromide.

Six experiments were carried out under the conditions given in the paper by Dewar and Jones. The aluminium bromide used was freshly prepared, (i) by treating aluminium powder with bromine and distilling off the aluminium bromide and (ii) by passing bromine over red-hot aluminium turnings. The result in each case was the production of benzaldehyde and anthracene without a trace of the hydrocarbon $C_{16}H_{12}$. It may therefore be taken as established that this hydrocarbon cannot be formed from benzene. Moreover, in a simple Friedel and Crafts' reaction, namely the formation of benzophenone, aluminium bromide was used instead of aluminium chloride without in any way affecting the final products of the reaction.

II. The Action of Nickel Carbonyl on Naphthalene in presence of Aluminium Chloride (referred to subsequently as Dewar and Jones' reaction).

The yield of the hydrocarbon was never more than 2 per cent. of the naphthalene taken, and whether the reaction took place in the cold or at 100° there was always formed a considerable amount of a tarry product.

III. *The Action of Methyl Chloride on Naphthalene in presence of Aluminium Chloride* (referred to subsequently as Bischoff's reaction).

The crystalline hydrocarbon prepared by this method melted at 181° , and its previously assumed identity with Dewar and Jones' hydrocarbon (m. p. 181°) was definitely proved by the fact that a mixture of the two melted at the same temperature.

Neither Dewar and Jones nor Bischoff had extended their investigations to the tarry residues left after the isolation of the crystalline hydrocarbon; the series of new substances obtained from the two tars and about to be described in this paper was found to be the same, thereby furnishing additional proof of the identity of the effects produced on naphthalene in each of the reactions II and III.

IV. *The Action of Aluminium Chloride alone on Naphthalene.*

During the course of the work connected with the testing of methods II and III it had been noticed that aluminium chloride and naphthalene, when mixed in equimolecular proportions and kept in sealed tubes or in flasks connected with calcium chloride tubes, darkened to a deep purple colour and that after four weeks a considerable amount of tar had been formed. Moreover, on heating such mixtures at 100° for periods varying from thirty minutes to six hours the tar was formed rapidly and yielded, not only a crystalline hydrocarbon melting at 181° , but also a further series of products in every way the same as those obtained in II and III.

Mixtures of this hydrocarbon with either Dewar and Jones' or with Bischoff's hydrocarbon did not affect the melting point of these, thus proving the identity of the three substances.

Hence it has been established that neither nickel carbonyl nor methyl chloride is essential to the reaction occurring between aluminium chloride and naphthalene, although the presence of nickel carbonyl has, at the ordinary temperature, an accelerating effect.

Friedel and Crafts (*Compt. rend.*, 1885, 100, 692) studied the action of aluminium chloride (1 part) on naphthalene (4 parts) and noticed that these two substances reacting at temperatures between 100° and 160° gave $\beta\beta$ -dinaphthyl, $C_{20}H_{14}$, melting at 187° , and a mixture of hydrodinaphthylenes. This value for the melting point of $\beta\beta$ -dinaphthyl was corroborated by Watson Smith. Friedel and Crafts found that $\beta\beta$ -dinaphthyl was not affected by heating with a further quantity of aluminium chloride, whereas the hydrodinaphthylenes were converted to hydronaphthalenes (b. p. = 210° circ./760 mm.). They apparently did not investigate the products of higher boiling point.

It therefore became necessary to ascertain whether the formula for

the hydrocarbon is $C_{16}H_{12}$ as proposed by Bischoff and accepted by Dewar and Jones, or $C_{20}H_{14}$ as given by Friedel and Crafts.

Dewar and Jones found $C = 93.7$ and 93.9 ; $H = 5.63$ and 5.76 .

$C_{16}H_{12}$ requires $C = 94.12$; $H = 5.88$.

$C_{20}H_{14}$ „ $C = 94.49$; $H = 5.51$ per cent.

It is obvious that for a compound containing so high a percentage of carbon, analysis alone furnishes insufficient evidence. Bischoff made no molecular weight determination, and the results obtained by Dewar and Jones varied considerably owing to the experimental difficulties due to the high boiling point and slight solubility of the substance.

Dewar and Jones found M.W. values varying between 180 and 263.

$C_{20}H_{14}$ requires M.W. = 254.

$C_{16}H_{12}$ „ M.W. = 204.

Study of the picrate supplied the data for the necessary decision. Bischoff had prepared a picrate of his hydrocarbon, and found its melting point to be 181° , whilst according to Watson Smith (Trans., 1885, 47, 104) the picrate of $\beta\beta$ -dinaphthyl melts at 183° . The picrates of the hydrocarbons prepared in the course of the present investigation according to methods II, III, and IV were in each case found to melt at 183° , and the analyses of these picrates (see experimental part) gave the formula $C_{20}H_{14} \cdot 2[C_6H_2(NO_2)_3 \cdot OH]$. Therefore the hydrocarbon under investigation must be taken not to have the formula $C_{16}H_{12}$, but $C_{20}H_{14}$, that of $\beta\beta$ -dinaphthyl. It must, however, be pointed out that all attempts to reconcile the value found for the melting point with 187° , that given by Friedel and Crafts, were unsuccessful; in spite of repeated recrystallisation from benzene and ethylene dibromide, the melting point remained constant at 181° (uncorr.).

The formation of the hydrocarbon thus recognised as $C_{20}H_{14}$, from naphthalene and aluminium chloride, which has been shown to be independent of the presence of either nickel carbonyl or methyl chloride, is therefore one of simple condensation.

Preparation and Investigation of Other Products formed in the Reaction between Naphthalene and Aluminium Chloride.

These products were studied in some detail and were neither hydrodinaphthylenes nor hydronaphthalenes, as had been obtained by Friedel and Crafts. The following substances were isolated:

(i) *From the fraction boiling at $215-225^\circ/10\text{mm.}$, a pale yellow oil.*

Analysis and molecular weight determinations gave for this substance the formula $C_{14}H_{10}$. The attempts to elucidate its constitution did not lead to conclusive results, although they afforded certain indications. The formation of a naphthalenecarboxylic acid points to a homologue of naphthalene. Moreover, it is known that the action of

aluminium chloride on benzene results in the production of alkyl-benzenes and diphenyl, whilst with homologues of benzene the mono-alkyl derivatives interact, yielding di- or tri-derivatives; hence it would seem justifiable to infer that the new substance $C_{14}H_{16}$, derived from naphthalene under conditions comparable to the above, is tetramethyl- or diethyl-naphthalene, more probably the former.

(ii) *From the fraction boiling above $300^{\circ}/10\text{mm.}$, a red, transparent, resinous, highly fluorescent solid.*—Analyses of this substance and of its nitro- and nitro-oxidation derivatives establish for it the formula $C_{26}H_{22}$ (see p. 1111). It is suggested that it is a homologue of dinaphth-anthracene, $C_{22}H_{14}$ (Russig, *J. pr. Chem.*, 1900, [ii], 62, 30):

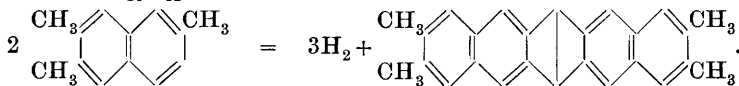


on the following grounds:

(a) The intense fluorescence of the substance suggests the presence of an anthracenoid linking which can be expressed in the above formula, thus leaving C_4H_8 to be accounted for by side chains.

(b) The actual presence of at least one alkyl side chain, probably methyl (see p. 1112), is indicated by the composition of the nitro-oxidation product.

(c) From the facts known of the action of aluminium chloride on benzene and its homologues already referred to above, it seems justifiable to infer that the condensation occurring here has resulted in the formation of a symmetrical product, namely, tetramethyl-dinaphthanthracene. During the course of the present investigation on naphthalene it has been demonstrated that besides $\beta\beta$ -dinaphthyl (substance B), there is also produced an alkylated naphthalene (substance A); under the influence of the aluminium salt the mono-alkylated naphthalenes probably first formed would be converted into di-, tri-, or tetra-alkylnaphthalene; and two molecules of the trimethyl derivative so produced might, in the presence of more aluminium chloride, condense with elimination of hydrogen to form the compound, $C_{26}H_{22}$, thus:



The fact that no alkyl derivatives of naphthalene other than substance A (identified as either diethyl- or tetramethylnaphthalene) have been isolated, and that the yield of A relatively to that of C, the supposed condensation product of the alkylated naphthalene, was always small, may be taken to lend some support to this interpretation of the reaction.

(iii) *From the residue left after vacuum distillation by fractional precipitation, a yellowish red solid.*—This does not distil in a vacuum at the temperature at which Jena glass softens. Analysis and molecular weight determinations of the substance itself and study of four bromo-derivatives would seem to prove conclusively that the formula is $C_{40}H_{26}$. It is probable that the compound is tetra-naphthyl and is formed by the condensation of either four naphthalene or two $\beta\beta$ -dinaphthyl molecules. The nature of the process has not been elucidated in the course of this investigation.

EXPERIMENTAL.

(1) Intimate mixtures of aluminium chloride (4 mols.) and naphthalene (4 mols.) were treated with nickel carbonyl (1 mol.) and left in sealed tubes for one to six hours at 100° , or were left in flasks connected with calcium chloride tubes at the ordinary temperature for ten to fourteen days (Dewar and Jones' reaction); (2) a slow current of methyl chloride was passed for two to three hours through a mixture of aluminium chloride (19 grams) and naphthalene (95 grams) kept between 80° and 90° (Bischoff's reaction); (3) mixtures of aluminium chloride (1 mol.) and naphthalene (1 mol.) in flasks connected with calcium chloride tubes were kept for one to three hours at 100° .

In each case the tarry residue was treated with water and hydrochloric acid, after which it was either allowed to cool and then separated by filtration into its solid and liquid constituents, or treated, while still hot, with benzene, and the extract so obtained dried over calcium chloride and distilled. The solid obtained by either method was then examined; after the rejection of the portions boiling below $260^\circ/760$ mm. and of any unchanged naphthalene, it was subjected to fractional distillation and subsequent fractional precipitation, when the following products were collected:

A. $215\text{--}225^\circ/10$ mm. Pale yellow oil, soluble in light petroleum and xylene.

B. $250\text{--}300^\circ/10$ mm. Viscid, deep yellow oil, solidifying to crystals melting at 181° , which in the cold are almost insoluble in light petroleum and xylene.

C. Above $300^\circ/10$ mm. Red, viscous oil, which on cooling sets to a brittle, resinous solid, becoming plastic at $49\text{--}50^\circ$, and is soluble in light petroleum and xylene.

D. A yellowish-red powder, soluble in xylene and insoluble in light petroleum, which is obtained from the residue left after the vacuum distillation by extracting with hot xylene and then precipitating with light petroleum. The repetition of this process yielded the solid in a pure condition.

The difference in solubility of the four substances *A*—*D* in xylene and light petroleum made it possible to devise other processes of separation of *B* from *A* and *C*, and of *C* from *D*; these processes, the details of which need not be given here, did not involve complete fractional distillation, and thus obviated the difficulty due to the tendency of the higher boiling constituents of the tar to decompose explosively.

The approximate percentage yield in terms of the original naphthalene was :

| | | |
|-----------|-------|--------|
| <i>A.</i> | 1 | impure |
| <i>B.</i> | 2—3 | „ |
| <i>C.</i> | 10—15 | „ |
| <i>D.</i> | 10—12 | „ |

Increase in the time allowed for the action of aluminium chloride on naphthalene, or rise in the temperature at which the reaction was conducted, caused a decrease in the amount of residual unchanged naphthalene, and an increase in the amount of *C* and *D* produced relatively to *A* and *B*.

Substance A.—This is a pale yellow oil with a very disagreeable odour, extremely soluble in ethylene dibromide, benzene, xylene, toluene, alcohol, light petroleum, ether, glacial acetic acid, or carbon disulphide. The pure oil, as obtained after many fractionations, could be kept for some three or four weeks without appreciable alteration in colour, but unless thus purified it darkened even in diffused light and became markedly fluorescent. Solutions, even of the pure substance, which were slightly fluorescent at first, soon darkened, and the fluorescence became intensely blue. The oil and its solutions showed no absorption band in the visible portion of the spectrum.

The mean values of six analyses varying from $C = 90.3$ to 91.6 , and $H = 7.74$ to 8.52 , and of five molecular weight determinations varying from 176 to 195 were :

$$C = 90.9 ; H = 8.09 ; M.W. = 186.$$

$$C_{14}H_{16} \text{ requires } C = 91.2 ; H = 8.8 \text{ per cent. ; } M.W. = 184.$$

There were indications of the formation of a picrate, of a bromine substitution derivative, and of an oxidation product due to the action of alkaline permanganate, but none of these derivatives could be isolated. The action of 10 per cent. nitric acid yielded an oxidation product, which was a crystalline acid free from nitrogen, melting with decomposition at $204-208^{\circ}$, giving the fluorescein test, and evolving naphthalene when heated with sodium. It may therefore be inferred that this oxidation product is a naphthalenecarboxylic acid. The very small amount of this substance available (less than 0.1 gram) was, through the silver salt, converted into the methyl ester, which,

after ten crystallisations from ether, was obtained in white needles with the constant melting point 119—120°, but could not be further investigated.

Substance B.—The yellow crystals purified by several recrystallisations from benzene, melted at 181° and possessed the properties fully described by Dewar and Jones. A spectroscopic examination of solutions showed absence of absorption bands in the visible portion of the spectrum. As already stated (p. 1106), the new work on this substance supplied evidence for assigning to it the formula $C_{20}H_{14}$ and identifying it with Friedel and Crafts' $\beta\beta$ -dinaphthyl.

The picrate was obtained by treating a benzene solution of 2.5 grams of the purified hydrocarbon with a benzene solution of 2.3 grams of picric acid, and recrystallising the resulting product from benzene until the melting point became constant at 183°.

0.26525 gave 0.5180 CO_2 and 0.0680 H_2O . $C = 53.3$; $H = 2.87$.

0.2240 „ 23.4 c.c. moist nitrogen at 17.5° and 761 mm. $N = 12.18$.

$C_{16}H_{12}, 2[C_6H_2(NO_2)_3 \cdot OH]$ requires $C = 50.05$; $H = 2.72$; $N = 12.7$
per cent.

$C_{20}H_{14}, 2[C_6H_2(NO_2)_3 \cdot OH]$ requires $C = 53.93$; $H = 2.79$; $N = 11.8$
per cent.

From these analyses it is clear that the formula for the picrate must be $C_{20}H_{14}, 2[C_6H_2(NO_2)_3 \cdot OH]$; hence the formula for the parent hydrocarbon is $C_{20}H_{14}$, and not $C_{16}H_{12}$, as had been previously assumed.

Some additional evidence for the $C_{20}H_{14}$ formula was obtained by the study of its quinones. By varying the proportions of the chromium trioxide used (1 mol. of $C_{20}H_{14}$ either to 8 or to 4 of CrO_3), two quinones differing in solubility and melting point were obtained. The one melting and decomposing at 250°, which is insoluble in alcohol but can be recrystallised from glacial acetic acid, exhibited the properties of the quinone described by Watson Smith (*loc. cit.*) and Chattaway (Trans., 1895, 67, 662), and gave on analysis numbers agreeing with the $\beta\beta$ -di- α -naphthaquinone formula $C_{20}H_{10}O_4$ which they assigned to it. The other quinone, which melts and decomposes at 161—167°, is very soluble in glacial acetic acid, but can be recrystallised from alcohol; it gave on analysis results in fair agreement with the formula $C_{20}H_{12}O_2$ for β -naphthyl-naphthaquinone (Chattaway, *loc. cit.*).

Substance C is a red, transparent solid with a green fluorescence. It is very soluble in benzene, toluene, xylene, light petroleum, ether, carbon disulphide, carbon tetrachloride, glacial acetic acid, ethylene dibromide, and to a less extent in alcohol. Its solutions show strong fluorescence of tints dependent on the concentration. This property is so marked that solutions containing one part of the solute in one

million of the solvent still exhibit fluorescence. The spectroscopic examination of this hydrocarbon, both in the visible and ultraviolet portions of the spectrum, yields results of considerable interest, which are still being investigated, and which will be dealt with in a subsequent paper. These results will be compared with those which may be obtained from a similar examination of dinaphthanthracene and of the hydrocarbons described in this paper. It is, however, pertinent to the present investigation to mention that dilute solutions show two characteristic absorption bands, the one in the blue, the other in the violet region. The following numbers were obtained on analysis:

0.2354 gave 0.8105 CO_2 and 0.1245 H_2O . $\text{C} = 93.9$; $\text{H} = 5.92$.

0.1570 „ 0.5395 CO_2 „ 0.0825 H_2O . $\text{C} = 93.71$; $\text{H} = 5.88$.

M.W. by cryoscopic method in (I) benzene, 344 and 317; (II) ethylene dibromide, 318.

$\text{C}_{26}\text{H}_{22}$ requires $\text{C} = 93.65$; $\text{H} = 6.35$ per cent. M.W. = 334.

There were indications of the formation of a picrate and of sulphonic acids, but in neither case could the product be isolated in a form suitable for analysis. Hydriodic acid was without effect. Whilst alkaline potassium permanganate produced no oxidation, chromium trioxide did so, but in this case also the yield was too small to allow of further investigation. Slightly better success attended the attempt to obtain bromine derivatives; a substitution product was isolated and analysed, but with results which showed that the substance so obtained was not quite pure. The action of fuming nitric acid (five to six parts to one of hydrocarbon), continued at the ordinary temperature for six days, resulted in the formation of a bright yellow nitro-compound, which was purified by precipitation from its chloroform solution by means of light petroleum. This nitro-compound melted at 167° .

0.1203 gave 0.2328 CO_2 and 0.0310 H_2O . $\text{C} = 52.8$; $\text{H} = 2.75$.

0.1000 „ 11.34 c.c. moist nitrogen at 16.3° and 755.5 mm. $\text{N} = 13.2$.

$\text{C}_{26}\text{H}_{16}(\text{NO}_2)_6$ requires $\text{C} = 51.7$; $\text{H} = 2.65$; $\text{N} = 13.9$ per cent.

The action of ordinary hot concentrated nitric acid yielded an oxidation product, less soluble in chloroform than the above, but sufficiently so to admit of its being purified in the same manner. The substance contained nitrogen; its solubility in sodium carbonate solution characterised it as an acid formed by the substitution of one or more carboxyl for alkyl groups, methyl, ethyl, &c.

0.1641 gave 0.3210 CO_2 and 0.0395 H_2O . $\text{C} = 53.35$; $\text{H} = 2.69$.

0.1774 „ 16.89 c.c. moist nitrogen at 14° and 761.2 mm. $\text{N} = 11.29$.

$\text{C}_{25}\text{H}_{14}(\text{NO}_2)_5 \cdot \text{CO}_2\text{H}$ requires $\text{C} = 53.0$; $\text{H} = 2.54$; $\text{N} = 11.9$ per cent.

$\text{C}_{24}\text{H}_{12}(\text{NO}_2)_5 \cdot \text{CO}_2\text{H}$ „ $\text{C} = 52.2$; $\text{H} = 2.26$; $\text{N} = 12.2$ „

The results obtained are therefore in fair agreement with the assumption that the above nitro-oxidation product had been formed by the introduction into the parent hydrocarbon $C_{26}H_{22}$ of five nitro-groups simultaneously with the substitution of one carboxyl for one methyl rather than for one ethyl group.

Substance D is a very light powder, reddish yellow in colour, insoluble in alcohol, glacial acetic acid, ether, or light petroleum, and very soluble in benzene, toluene, xylene, ethylene dibromide, carbon tetrachloride, carbon disulphide or chloroform. A spectroscopic examination of the substance showed that strong solutions exhibit general absorption, but even in the case of dilute solutions there was no evidence of absorption bands in the visible region of the spectrum. It has not been obtained in a crystalline condition, as it tends to separate from its solutions as a tarry mass unless prepared as described in the earlier part of this paper. The melting point of the amorphous powder cannot be readily taken, as it darkens at about $190-200^{\circ}$ and at higher temperatures melts to a tar. Although it could not be obtained crystalline, it was considered as a definite, pure substance, since fractional precipitation had been continued until analyses of samples prepared at different times indicated constancy of composition.

0.1363 gave 0.4728 CO_2 and 0.0660 H_2O . $C = 94.7$; $H = 5.41$.

0.1978 „ 0.6826 CO_2 and 0.0948 H_2O . $C = 94.1$; $H = 5.37$.

0.2348 „ 0.8190 CO_2 and 0.1159 H_2O . $C = 95.0$; $H = 5.53$.

M.W. by cryoscopic method in (I) benzene, 524, (II) ethylene dibromide 473 and 517.

$C_{40}H_{26}$ requires $C = 94.8$; $H = 5.19$ per cent. M.W. = 506.

There were indications of the formation of a picrate, of sulphonic acids and of a nitro-derivative, but in no case were the products suitable for further investigation. Alkaline permanganate, chromium trioxide and ten per cent. nitric acid were without action on the substance.

Further evidence as to the formula for the hydrocarbon was, however, furnished by the analysis of a series of four bromo-substitution products formed by the action of the calculated quantities of bromine on the hydrocarbon in carbon tetrachloride solution. The resulting products were too soluble in benzene, xylene, toluene or carbon tetrachloride to be purified by crystallisation. An attempt was therefore made to obtain them pure by fractional precipitation from their benzene solutions by the addition of alcohol, in which they are almost insoluble. The process was repeated several times, but complete separation from the higher or lower bromo-derivatives was not effected. Hence the analyses do not show perfect agreement with the theoretical numbers; the discrepancies however are not so great but that the

results may be taken to support the formula $C_{40}H_{26}$ for the parent hydrocarbon.

(I) 1 Molecule of $C_{40}H_{26}$: 2 Molecules of Bromine.

0.1961 gave 0.5091 CO_2 and 0.0700 H_2O . $C = 70.7$; $H = 4.00$.

0.2198 „ 0.1280 AgBr. $Br = 24.8$.

$C_{40}H_{24}Br_2$ requires $C = 72.3$; $H = 3.6$; $Br = 24.1$ per cent.

(II) 1 Molecule of $C_{40}H_{26}$: 3 Molecules of Bromine.

0.1918 gave 0.4515 CO_2 and 0.0570 H_2O . $C = 64.2$; $H = 3.33$.

0.2170 „ 0.1704 AgBr. $Br = 33.4$.

0.1157 „ 0.0877 AgBr. $Br = 32.2$.

$C_{40}H_{23}Br_3$ requires $C = 64.6$; $H = 3.1$; $Br = 32.3$ per cent.

(III) 1 Molecule of $C_{40}H_{26}$: 4 Molecules of Bromine.

0.2023 gave 0.4368 CO_2 and 0.0647 H_2O . $C = 58.88$; $H = 3.3$.

0.2010 „ 0.1853 AgBr. $Br = 39.2$.

$C_{40}H_{22}Br_4$ requires $C = 58.4$; $H = 2.7$; $Br = 38.9$ per cent.

(IV) 1 Molecule of $C_{40}H_{26}$: 5 Molecules of Bromine.

0.2808 gave 0.5313 CO_2 and 0.0665 H_2O . $C = 51.7$; $H = 2.65$.

0.2657 „ 0.2779 AgBr. $Br = 44.6$.

0.2870 „ 0.3061 AgBr. $Br = 45.4$.

$C_{40}H_{21}Br_5$ requires $C = 53.3$; $H = 2.3$; $Br = 44.4$ per cent.

Summary :

(I) The hydrocarbon to which Bischoff had assigned the formula $C_{16}H_{12}$ cannot be obtained from benzene. Its formation in Dewar and Jones' and Bischoff's reactions respectively does not depend on the presence of either nickel carbonyl or methyl chloride, but is merely due to the condensing effect of aluminium chloride on naphthalene.

(II) This hydrocarbon has not the formula $C_{16}H_{12}$, but is identical with Friedel and Crafts' $\beta\beta$ -dinaphthyl, $C_{20}H_{14}$, formed by a process of simple condensation.

(III) The specific effect of aluminium bromide in the above, as in other Friedel and Crafts' reactions, is the same as that of aluminium chloride.

(IV) From the product of the reaction between aluminium chloride and naphthalene, besides $\beta\beta$ -dinaphthyl, there have also been isolated three new hydrocarbons :

1114 PERMAN AND DAVIES: MOLECULAR WEIGHT OF

(1) $C_{14}H_{16}$, a homologue of naphthalene, probably tetramethyl- or diethylnaphthalene.

(2) $C_{26}H_{22}$, a substance with interesting spectroscopic properties probably a homologue of dinaphthanthracene $C_{22}H_{14}$.

(3) $C_{40}H_{26}$, which is probably tetranaphthyl formed by a process of condensation.

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