Two-stage benzylation. Calculated for $C_{12}H_{16}O_{10}(C_7H_7)_4$: C, 70.17; H, 6.58. Found: C, 69.74; H, 6.32.

It does not appear probable that the product showing the composition of tribenzyl cellulose is a mixture of di- and tetrabenzyl derivatives. The mono benzyl compound did not show signs of softening when heated to 250°, the tribenzyl substance melted at 208° to 10°, while the tetra benzyl compound softened at 165°, and melted at 175° to 77°. The tribenzyl substance appeared as fully insoluble in the various organic solvents as the monobenzyl derivative, while the tetrabenzyl cellulose proved soluble in chlorohydrin, chloroform, nitrobenzene, ethyl acetate, and was gelatinized by acetone.

The three benzyl derivatives do not reduce Fehling's solution. On treating with dilute acid, the monobenzyl and the tribenzyl compounds yield after 1 hour soluble reducing carbohydrates, while tetrabenzyl cellulose does not do so even after two hours' heating. None of the three substances is soluble in cold conc. hydrochloric acid, and the latter contains no reducing carbohydrates after 2 hours' contact with the products, and shows but a slight reduction after two days' standing.

## Summary.

It has been shown that carbohydrates of all types are readily benzylated, and various benzyl ethers obtained are described. The benzylation reaction should prove useful in the further study of carbohydrates, just as alkylation by means of methyl sulfate has proven so preëminently fruitful in this field. Moreover, some of the benzyl ethers of the carbohydrates may prove, it is hoped, technically useful products because of their properties as colloid and plastic substances, particularly since benzyl chloride is relatively inexpensive and the group increases considerably the molecular weights of the carbohydrates to which it adds.

ANN ARBOR, MICH.

# THE QUANTITATIVE DETERMINATION OF PHENANTHRENE.[1]

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The hydrocarbon phenanthrene has been the object of much research. It occurs in relative abundance in coal tar along with carbazole and anthracene, being isomeric with the latter. Much work has naturally been directed toward using it in making dyes and, indeed, many patents have been granted for dyes of which it forms a basis. Notable among such dyes is flavinduline. Further, the morphine alkaloids contain a phenanthrene nucleus, and this fact has been most potent in giving impulse to investiga-

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[1] Read before the Dye Division of the American Chemical Society at the Rochester Meeting, April, 1921.

* Died September 1, 1921.

tion of the chemistry of the hydrocarbon and of its derivatives. It will be clear that an adequate method of determining it is desirable.

In spite of the fact that the constituents of coal tar have interested chemists for many years past, there are comparatively few of these constituents for which accurate quantitative methods have been worked out,— methods comparable to that for anthracene, for example, and applicable in the presence of the usual accompanying substances. Thus we are still compelled to determine carbazole by first removing bases, then determining the remaining nitrogen and calculating it as carbazole. For naphthalene there is no chemical method at all comparable to that for anthracene, though the chemistry of the former early reached a high stateof development. Highly accurate methods of determination then are almost everywhere lacking among the coal-tar constituents, even including benzene and toluene. It is not surprising, therefore, that for phenanthrene, which has only just begun to receive commercial development in this country, there should have been wanting an adequate mode of quantitative estimation.

Historical.—Record of essentially but one method of analysis appears in the literature.[2] In one variation the hydrocarbon is precipitated as the picrate from an alcoholic solution. The phenanthrene is then regenerated and washed with sulfuric acid to remove acridine. Allowance is made for the phenanthrene picrate remaining dissolved in the mother liquors. In the other variation[3] the hydrocarbon is precipitated as the picrate from xylene solution. An allowance is made for the amount of "rough picrate" remaining dissolved in the xylene mother liquor. A weighed portion of the precipitated "rough picrate" from the xylene is then recrystallized from 95% alcohol and a correction (20 g. of picrate for 750 cc. of 95% alcohol) applied in order to allow for the picrate remaining dissolved in the alcoholic mother liquors.

Küster[4] attempted the estimation of phenanthrene by conversion to the picrate by means of an aqueous solution of picric acid, but without success.

Obviously any attempt to determine phenanthrene by means of picric acid in the presence of the usual coal-tar accompaniments is seriously handicapped by two factors, (1) the relatively large solubility corrections that have to be applied, and (2) the fact that the most important anthracene-oil accompaniments of phenanthrene also form picrates of about the same order of solubility. Thus, for example, anthracene, carbazole, and fluorene all form picrates.

Analysis of the Problem.—The problem resolved itself, in view of the recorded chemistry of the compound, into (1) the quantitative oxidation of the hydrocarbon to the quinone, and (2) the quantitative estimation of the quinone produced.

[2] Anschütz and Schultz, *Ann.*, **196**, 43 (1879).

[3] Lunge's "Coal Tar and Ammonia," Pub. D. Van Nostrand Co., 4th Ed., 1916, p. 643.

[4] Küster, *Ber.*, **27**, 1104 (1894).

It was found convenient to solve the second part of the problem first in order to make it easy to follow progress in working out the first part.

## Experimental.

**Quantitative Determination of Phenanthraquinone.**—For this second aspect of the problem a solution lay already in view inasmuch as phenanthraquinone, as an *ortho*-diketone, forms generally well defined, rather insoluble compounds, azines, with *ortho*-diamines.  3,4-tolylene diamine was chosen as precipitant both because it forms with phenanthraquinone a well defined, sufficiently insoluble azine,[5] toluphenanthrazine, and because it is an easily obtainable *ortho*-diamine.[6]  Moreover, the precipitation takes place very well in glacial acetic acid and since it was proposed to carry out the oxidation of phenanthrene also in glacial acetic solution, this fact was of great assistance.  To be carried out, therefore, in connection with the second aspect of the problem, there remained for the most part only the obtaining of quantitative data regarding the precipitation, data by means of which progress in much of the search for a quantitative oxidant was followed.

*Experiment 1.*—One-fourth g. of phenanthraquinone (m. p. 203°) was dissolved in 25 cc. of glacial acetic acid.   To the cold solution 0.60 g. of 3,4-tolylene-diamine was added.   After standing in running tap water overnight, the precipitated toluphenanthrazine was filtered on a weighed Gooch crucible and washed with water.   Yield, 0.3043 g., or 86.1%; m. p., 217° (uncorr.).

*Experiment 2.*—Another experiment in which only 0.28 g. of base was added and where the system stood in tap water only 30 to 40 min. resulted in a yield of 0.2979 g. of precipitate, or 84.5%.   The precipitate was washed in this case, first with 50% acetic solution and then with water.

*Experiment 3.*—A third experiment was carried out as follows.   0.2500 g. of the quinone was dissolved in 25 cc. of glacial acetic acid in a 50cc. Erlenmeyer flask.   0.7407 g. of iodic acid (the oxidant for phenanthrene later found most suitable) was added and the solution was boiled under an air condenser for 2½ hours.   No free iodine appeared. After standing overnight in tap water, the solution was filtered through a Gooch crucible into another Erlenmeyer flask and the residue of iodic acid washed with glacial acetic acid.   Inasmuch as a slight sediment appeared in the filtrate (perhaps asbestos from the filter mat), the solution was distilled to less than 25 cc., then made up to 25 cc. and allowed to stand in running tap water overnight.   The solution was again filtered, distilled to less than 25 cc. and made up again to 25 cc.   0.60 g. of base was added and, after standing in running tap water overnight, the precipitate was filtered off.   It weighed 0.3026 g. an 85.6% yield; m. p., 215.5° to 216.6° (uncorr.).

The average yield in these three experiments is 85.4%, but 85.0% was taken for subsequent calculations as being within the experimental error in practical application.   The theoretical weight of toluphenanthrazine from 0.2500 g. of phenanthraquinone is 0.3535 g.   The solu-

[5] Hinsberg, *Ber.*, **18**, 1228 (1885); *Ann.*, **237**, 341 (1887).

[6] Gattermann, *Ber.*, **18**, 1483 (1885); Kleemann, *ibid.*, **19**, 336 (1886); Beilstein and Kuhlberg, *Ann.*, **158**, 351 (1871).

bility of toluphenanthrazine in 25 cc. of glacial acetic acid is, for practical purposes, represented by $(100 - 85 =) \ 15\%$ of 0.3535 g., or 0.0530 g. This latter weight, then, since precipitation was always performed in 25 cc. of solution, was always added as a correction to the weight of the azine precipitated.

The three experiments described above further indicate that the amount of base added is without material influence on the result and that iodic acid does not destroy phenanthraquinone under the conditions.

Another base, 1-ethoxy-3,4-diaminobenzene[7] was later tried and found to precipitate 91.3% of 0.2500 g. of phenanthraquinone under conditions as above described. Washing in this case was first performed with 25 cc. of a 50% acetic acid solution saturated with $p$-ethoxy-phenanthrazine,[8] the product precipitated, and finally with water. This diamine was not further experimented with, however, inasmuch as considerable data were already at hand based on the use of 3,4-tolylenediamine.

**The Quantitative Oxidation of Phenanthrene.**—Many substances were tried in the course of the search for a quantitative oxidant for phenanthrene. Among the substances which, judging in some cases only by the appearance of yellow color, resulted in the formation of phenanthraquinone when boiled with a glacial acetic acid solution of phenanthrene, were lead dioxide, manganese dioxide (upon the addition of a few cubic centimeters of 1-1 sulfuric acid), hydrogen peroxide, potassium chlorate, potassium bromate, potassium iodate, and iodic acid. Chromic acid was not experimented with since it is known to have a destructive action on phenanthraquinone. The search finally narrowed down to the potassium halates and from these to iodic acid, which alone was found to be suitable. Potassium bromate was found to be much quicker in action than iodic acid but it also had a destructive effect on phenanthraquinone. For example, after boiling a solution of 0.2500 g. of the quinone in 25 cc. of glacial acetic acid for $2\frac{1}{2}$ hours with 0.80 g. of potassium bromate, but 59.7% of the quinone was precipitable as toluphenanthrazine.

Experiments according to the Höchst test with iodic acid were carried out using a sample of phenanthrene (A) containing 8.4% of anthracene[9] and no doubt other impurities, although it was a pure white material of excellent appearance. In each of these experiments a solution of 0.2500 g. of the hydrocarbon in 25 cc. of glacial acetic acid, contained in a 50cc. Erlenmeyer flask, was boiled with 0.74 g. of iodic acid under an air condenser for the time specified. Each flask was then allowed to stand in running tapwater overnight, after which the excess of iodic acid

[7] Autenrieth and Hinsberg, *Arch. Pharm.*, **229**, 456 (1891).

[8] Autenrieth and Hinsberg, *Ber.*, **25**, 497 (1892).

[9] Essentially as described in Lunge's "Chem.-tech. Untersuchungsmethoden," Julius Springer, Berlin, 4th Edition, Vol. II, p. 740.

was filtered through a Gooch crucible (mat dry, or wet with acetic acid) into another Erlenmeyer flask (a 100cc. flask is most conveniently used) and washed with glacial acetic acid. The filtrate was evaporated to slightly less than 25 cc. and then made up to exactly 25 cc. by comparison with a similar flask containing 25 cc. of water. When the contents of the flask were cool, 0.60 g. of the base was added. After standing overnight, the precipitate was filtered on a weighed Gooch crucible and washed first with 25 cc. of 50% acetic acid and then with water. The solubility correction of 0.0530 g. was added in each case and the percentage of phenanthrene calculated. The factor for the conversion of toluphenanthrazine to phenanthrene is 0.6052.

The results of five experiments are tabulated as follows.

| Expt. | Boiling time. Hours. | Wt. of precipitate. G. | Phenanthrene indicated. %. | Remarks. |
|---|---|---|---|---|
| 4 | 0.5 | 0.0838 | 33.1 | m. p. of ppt. 213.5°. (uncorr.) |
| 5 | 2.0 | 0.2927 | 83.7 | m. p. of ppt. 213°–213.5°. (uncorr.) |
| 6 | 2.5 | 0.2949 | 84.2 | |
| 7 | 2.5 or 3.5 | 0.2958 | 84.4 | Boiling time probably 2½ hrs. |
| 8 | 3.0 | 0.2924 | 83.6 | |

The results of four similar experiments with a much purer phenanthrene, (B), melting at 99.6° follow. They differ only in that 0.75 g. of iodic acid and 1.00 g. of base were used and in that the 50% acetic acid wash solution was saturated with toluphenanthrazine, variations having little or no effect on the results.

| Expt. | Boiling time. Hours. | Wt. of precipitate. G. | Phenanthrene indicated. %. |
|---|---|---|---|
| 9 | 2.5 | 0.3359 | 94.1 |
| 10 | 2.5 | 0.3367 | 94.2 |
| 11 | 3.0 | 0.3356 | 94.1 |
| 12 | 3.75 | 0.3352 | 94.0 |

The preceding nine experiments, together with Expt. 3, show that phenanthraquinone in acetic acid solution is not attacked by iodic acid and they indicate that 2½ hours' boiling results in a quantitative oxidation of the phenanthrene, inasmuch as longer boiling times do not cause any further alteration in the phenanthrene content found.

That a quantitative oxidation of phenanthrene had been attained was further shown by the results of analyses of mixtures of the 84.2% phenanthrene (A), with a high purity anthracene (C), with an anthracene of lower grade (D), and with an analyzed crude phenanthrene (E). Sample C melted at 216° and analyzed 97.05% anthracene; Sample D was a technical product of 88.7% purity, and Sample E analyzed 68.4% phenanthrene (see Expts. 18 and 19). The following tabulation and remarks present the results of these experiments and detail any varia-

tions in procedure.  The duration of oxidation in each experiment was 2½ hours.  0.60 g. of base was used each time.

| Expt. | Composition of sample. | Wt. of HIO₃. G. | Wt. of precipitate. G. | Phenanthrene. Found. %. | Calc. %. |
|---|---|---|---|---|---|
| 13 | 0.2500 g. of Anth. C | 1.5 | 0.2744 | 39 6 | 42.1 |
|  | +0.2500 g. of Phen. A |  |  |  |  |
| 14 | " | 1.5 | 0.2771 | 39.9$^a$ | 42.1 |
| 15 | 0.8000 g. of Anth. C | 2.0 | 0.2110 | 16.0$^a$ | 16.8 |
|  | +0.2000 g. of Phen. A |  |  |  |  |
| 16 | 0.1250 g. of Anth. D | 0.75 | 0.1348 | 45.5 | 42.1+$x$ |
|  | +0.1250 g. of Phen. A |  |  |  |  |
| 17 | 0.1250 g. of Phen. E | 0.75 | 0.2634 | 76.6 | 76.3 |
|  | +0.1250 g. of Phen. A |  |  |  |  |

$^a$ The somewhat low results may indicate the desirability of longer oxidation time in the case of materials high in anthracene.

REMARKS.—*Expts. 13, 14, and 15:* Oxidized in 50 cc. of glacial acetic acid; let stand 48 hours in running water; filtered off precipitated anthraquinone, washing with glacial acetic acid; distilled to 20 cc.; let stand overnight in running water; filtered off slight brownish deposit of impure anthraquinone, washed with glacial acteic acid; distilled to 25 cc.; cooled; added base; let stand overnight in running water.

*Expt. 16:* Oxidized in 25 cc. of glacial acetic acid; let stand overnight in running water; filtered off the precipitated anthraquinone, washing with glacial acetic acid; distilled to about 18 cc.; let stand overnight in running water; filtered, washing with glacial acetic acid; distilled to 25 cc.; cooled; added base; let stand in running water overnight.  $x = \%$ of phenanthrene from Sample D, doubtless not more than a few per cent.

*Expt. 17:* Similar to 16 except that there was but one distillation.

Anthracene also is oxidized to the quinone by iodic acid, hence the necessity of the procedure followed in the preceding five experiments directed toward removing anthraquinone.  This separation is possible because of the very considerably lower solubility of anthraquinone in glacial acetic acid as compared with phenanthraquinone.

Both potassium bromate and iodic acid in glacial acetic acid are excellent oxidants for anthracene.  Boiling 0.2500 g. of a 97.0% anthracene in 25 cc. of glacial acetic acid for 5 minutes with 0.70 g. of potassium bromate resulted in an oxidation of 74.1% of the anthracene. . Boiling 1.0000 g. in 50 cc. for 20 minutes with 2.5 g. of potassium bromate resulted in an oxidation of 92.8% and 89.8% (2 samples).  Boiling 1.0000 g. in 50 cc. for 2½ hours with 3.00 g. of iodic acid resulted in an oxidation of 98.4% and 98.3% of the anthracene (2 samples).  Following oxidation, the determination of the anthraquinone produced was accomplished as in the Höchst procedure for anthracene.  Potassium bromate and iodic acid are probably quantitative oxidants for this hydrocarbon.

**Examples of Application of the Method.**—The phenanthrene was determined on three specimens of crude phenanthrene.  The first was the material (E) referred to above, the second (F) was essentially the

phenanthrene fraction from a column distillation (plant scale) of an anthracene oil and was an oily solid, while the third (G) was the press-cake obtained from Sample F by pressing in a letter-press between folds of filter paper. 0.60 g. of base and 0.74 g. of iodic acid were used in each determination.

| Expt. | Material. G. | Wt. of precipitate. G. | Phenanthrene. %. |
|---|---|---|---|
| 18 | 0.2500 (E) | 0.2290 | 68.26 |
| 19 | " | 0.2304 | 68.61 |
| 20 | 0.2500 (F) | 0.2097 | 60.8 |
| 21 | " | 0.2151 | 61.9 |
| 22 | 0.2500 (G) | 0.2643 | 76.8 |
| 23 | " | 0.2589 | 75.5 |

REMARKS.—*Expts. 18 and 19:* Oxidized in 25 cc. glacial acetic acid; cooled; filtered, washing with glacial acetic acid; distilled to 25 cc.; cooled; added base; let stand overnight; filtered, washed with 25 cc. of 50% acetic acid saturated with toluphenanthrazine, and with water.

*Expts. 20 and 21:* Oxidized in 20 cc. of glacial acetic acid; let stand overnight; filtered, washed with glacial acetic acid; distilled to 18–20 cc.; let stand overnight; filtered, washed with glacial acetic acid; distilled to 25 cc.; cooled; added base; finished as for No. 18.

*Expt. No. 22:* Same as for Expts. 20 and 21, except that material received but one distillation.

*Expt. No. 23:* Same as for Expts. 20 and 21.

In the hands of two other persons, Sample F gave the following results: 60.8%, 58.4%, average 59.6%; 61.2%, 60.3%, average 60.8%. These results represented their first experience with the method.

**Material Suited to Analysis.**—The method of analysis for phenanthrene employed in the preceding experiments is, in general, suitable for mixtures of anthracene-oil hydrocarbons 30% or higher in phenanthrene, containing less than 10% of carbazole, and containing no large amounts of the anthracene-oil constituents boiling above 360°. Cruder material requires preparation directed toward lowering the carbazole content and toward removing the high-boiling constituents. The method is best suited for crude and refined phenanthrenes and phenanthraquinones. It has been applied with satisfactory results directly to the phenanthrene range of distillates from a plant column distillation of anthracene oil.

Carbazole, if present in amounts exceeding perhaps 10%, interferes in the determination of phenanthrene. An oxidation product apparently is formed. This product is colored and behaves rather like a quinone. It will be further investigated. Fluorene does not interfere since it is not attacked. Acenaphthene, also, does not interfere because the quinone, if formed, gives a rather soluble azine. Moreover, acenaphthene is not likely to occur in any considerable proportion along with phenanthrene. In any event, the two hydrocarbons can be separated by distillation. Some

of the high-boiling coal-tar constituents interfere and a crude anthracene cannot be directly analyzed. Anthracene does not interfere since the anthraquinone formed may be filtered off from a smaller volume than that in which it is intended to precipitate the phenanthraquinone.

## Formal Analytical Procedure.

For materials containing 30% or more of phenanthrene, weigh out a 0.2500g. sample into a 50cc. Erlenmeyer flask. Add 0.75 g. of iodic acid and 20 cc. of glacial acetic acid. Fit a plain 90cm. air condenser to the flask and boil for 2½ hours at such a rate that the ring of iodine which usually condenses in the tube stands about 60 cm. from the flask. Cool, preferably for several hours, especially if anthraquinone separates, and then filter with gentle suction into a 100cc. Erlenmeyer flask through a Gooch crucible. A glass filter funnel (so-called carbon filter) is best used to hold the crucible. The oxidation mixture should be so slowly poured into the crucible that only a minimum amount of wash liquid need be used. Wash with glacial acetic acid. Fit the flask to a small empty Hempel distilling tube and distil to a volume *slightly* less than 25 cc. Some iodine will be carried over. By treating a portion of the distillate with a sodium thiosulfate solution, the color of the iodine may be removed in order to obtain assurance that no quinone has been carried over. Remove the Erlenmeyer flask and while the liquid is still warm make the volume (by comparison) up to 25 cc., as exactly as possible, with glacial acetic acid. Cool. Add 1.00 g. of 3,4-tolylene-diamine and swirl the flask until it has dissolved. A darkening, due to the action of iodine, will occur when the diamine is added. Set the flask in running water (at about 20°) overnight. Filter through a weighed Gooch crucible, using 25 cc. of a 50% glacial acetic acid solution saturated with toluphenanthrazine in transferring the precipitate and in the first part of the washing on the filter. Finally, wash with 200 cc. of cold water, dry the precipitate, and weigh. To the weight of the toluphenanthrazine add 0.0530 g., the weight of toluphenanthrazine remaining dissolved in the mother liquor. Multiply the sum by 0.6052, the factor for the conversion of toluphenanthrazine to phenanthrene, and calculate the percentage of the latter.

If the anthracene content exceeds a certain percentage (probably not under 15%, but perhaps considerably higher) anthraquinone may crystallize on cooling after oxidation. This will not interfere unless it is necessary to use so much acetic acid for washing that enough anthraquinone is dissolved to come down again when the volume is reduced to 25 cc. If, following distillation, it should crystallize out on cooling and making the volume up to 25 cc., further distillation to about 20 cc., cooling, refiltration, redistillation, etc,, will be necessary.

With certain materials low in phenanthrene, it is practicable to weigh out 0.5000g. samples and oxidize in 50 cc. of glacial acetic acid with 1.50 g. of iodic acid. In such cases, the first distillation is carried to less than 25 cc. and the solution is allowed to cool and stand. It is then filtered again, distilled, etc., and precipitation is performed in 25 cc., as usual.

## The Qualitative Determination of Phenanthrene.

Phenanthrene may be very conveniently determined qualitatively in the following manner. Oxidize the material to be tested as for quantitative determination. Cool; filter; pour the filtrate into water; filter; wash with water. Warm the residue with conc. sodium hydrogen sulfite solution. Filter and transfer the filtrate to a small separatory funnel. Wash with one or two portions of carbon tetrachloride to remove any accompanying hydrocarbons. Add a small portion of fresh carbon tetrachloride and acidify with hydrochloric acid containing ferric chloride to prevent the reduction of the liberated phenanthraquinone. Collect the quinone in the carbon tetrachloride and, first drying the spout of the funnel, draw off the carbon tetrachloride, which contains the quinone, and test by the reaction of Hilpert and Wolf.[10] The solution of the quinone is heated to boiling and there are added a few drops of a solution of 1 volume of antimony pentachloride in 2 volumes of carbon tetrachloride. A purple-red precipitate indicates phenanthraquinone and hence phenanthrene. Anthraquinone, which gives a cinnabar-red color with this reagent, cannot interfere because it would not be present, nor can acenaphthenequinone because it gives an apple-green precipitate. Fluorenone, which gives an orange precipitate, turning to reddish-orange, also would not be present.

## Summary.

Phenanthrene may be determined quantitatively by oxidation in glacial acetic acid by means of iodic acid to phenanthraquinone followed by precipitation of the quinone produced by means of 3,4-tolylene-diamine.

A procedure for the qualitative detection of phenanthrene is described.

NEW YORK, N. Y.

[10] Hilpert and Wolf, *Ber.*, **46**, 2217 (1913).