Anal. Calcd. for $C_{11}H_{11}O_2N_3$: C, 60.83; H, 5.07; N, 19.30; OCH_3, 0. Found: C, 60.86; H, 4.92; N, 19.56; OCH_3, 0.

Monomethyl Derivative (V).—Five-tenths gram of substance III was heated with 2 cc. of normal sodium hydroxide for ten minutes. After cooling the solution was acidified with dilute sulfuric acid; the product separated at once and was recrystallized from dilute methanol or from a large amount of water, as prismatic glistening white needles, of m. p. 278–280°. The same product was also obtained by heating substance III in aqueous or alcoholic hydrochloric acid.

Anal. Calcd. for $C_{10}H_9N_3O_2$: C, 59.11; H, 4.43; N, 20.49; OCH_3, 0. Found: C, 59.02; H, 4.54; N, 20.22; OCH_3, 0.

Alkali Hydrolysis of Substance IV.—Hydrolysis was carried out in an apparatus similar to that described by Lieber and Smith:[10] 217 mg. of substance III was dissolved in 40 cc. of 25% sodium hydroxide and heated. After the given time intervals the receiver containing a measured amount of acid was changed and the liquid in the distilling flask each time filled up to the original volume The acid was titrated with 0.1 *N* alkali and from the amounts used by the distilled ammonia and methylamine the percentage hydrolysis was computed. It was 36.7, 56.3, 73.0, 83.2, and 84.6% after one, two, four, six, and eight hours, respectively.

After eight hours the alkaline solution was carefully acidified and the resulting precipitate filtered. After recrystallization from alcohol the substance formed shining plates which proved to be identical in melting point and gave no melting point depression with benzoic acid (122°). In order to determine the nature of the distilling amine, 1 g. of substance IV was hydrolyzed for eight hours with 50 cc. of 25% potassium hydroxide and the distillate absorbed in excess hydrochloric acid. The solution was evaporated to dryness and the residue carefully dried in a vacuum desiccator to constant weight; yield 460 mg. The material was extracted in a Soxhlet extractor with absolute alcohol for four hours. The alcoholic extract on evaporation yielded 350 mg. of methylamine hydrochloride. The residue in the thimble consisted of ammonium chloride.

Reaction of Substance IV with Bromine.—Forty-five hundredths gram of substance IV was dissolved in 2 cc. of glacial acetic acid and 2.5 cc. of an 8% solution of bromine in glacial acetic acid added dropwise. The bromide crystallized at once in beautiful red plates, which on filtering and washing with dry ether became yellow, apparently with loss of hydrobromic acid; yield 0.57 g. The substance was recrystallized from hot glacial acetic acid, containing bromine; it is very soluble in methanol, ethanol, soluble in hot chloroform and glacial acetic acid, insoluble in ether; it is readily debrominated by dilute alkali, also by silver salts in aqueous solution or etheric suspension.

Anal. Calcd. for $C_{11}H_{11}O_2N_3Br_4$: C, 24.58; H, 2.04; N, 7.82; Br, 59.59. Found: C, 24.84; H, 2.30; N, 7.73; Br, 59.87.

Summary

2-Phenyl-4,6-dioxotetrahydrotriazine, the cyclization product of benzoyl biuret, yields two isomeric dimethyl derivatives on methylation with diazomethane. The pair represents a case of lactam–lactim tautomerism involving one of the two methyl groups.

NEW YORK, N. Y.

RECEIVED APRIL 18, 1938

[10] E. Lieber and G. B. L. Smith, THIS JOURNAL, **59**, 2283 (1937).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A New Synthesis of 3,4-Benzpyrene Derivatives

BY LOUIS F. FIESER AND E. B. HERSHBERG[1]

The only synthesis of the powerfully carcinogenic 3,4-benzpyrene heretofore achieved is that of Cook and Hewett,[2] consisting in the application to pyrene of the general method of constructing an additional ring with the use of succinic anhydride. With the technical improvements in the various steps introduced in this Laboratory,[3,4] by Winterstein, Vetter and Schön,[5] and by Vollmann, *et al.*,[6,7] 3,4-benzpyrene can now be prepared fairly readily by this method in over-all yield of about 36%.[3] The succinic anhydride synthesis, however, is not adaptable to the preparation of many derivatives of the important parent hydrocarbon, and the list of compounds thus far obtained by application of the general synthesis or by utilization of the same intermediates includes only the following substances: 4′-methyl-3,4-benzypyrene[3,8] (and its dihydride[3,8]), 3′(?)-methyl-3,4-benzpyrene,[5] 4′-hydroxy-3,4-benzpyrene,[4] 3,4-benzpyrene-3′,4′-dicarboxylic anhydride[9] (and its dihydride[9]), 1′,2′,3′,4′-tetrahydro-3,4-benzpyrene.[3,5,10]

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[1] Lilly Research Fellow.

[2] Cook and Hewett, *J. Chem. Soc.*, 398 (1933).

[3] L. F. Fieser and M. Fieser, THIS JOURNAL, **57**, 782 (1935).

[4] Fieser, Hershberg, Long and Newman, *ibid.*, **59**, 475 (1937).

[5] Winterstein, Vetter and Schön, *Ber.*, **68**, 1079 (1935).

[6] Vollmann, Becker, Corell and Streeck, *Ann.*, **531**, 1 (1937).

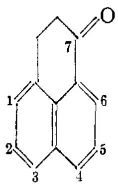
[7] For further comments on the synthesis, see Sannié and Poremski, *Bull. soc. chim.*, [5] **3**, 1139 (1936); Rondoni and Corbellini, *Atti accad. Lincei*, VI, **21**, 128 (1935).

[8] Fieser and Newman, THIS JOURNAL, **57**, 1602 (1935).

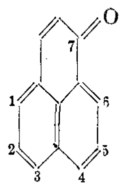
[9] L. F. Fieser, M. Fieser and E. B. Hershberg, *ibid.*, **58**, 1463 (1936).

[10] The analytical sample of this hydrocarbon prepared with Mrs. Fieser[3] (by Clemmensen reduction) formed faintly yellow plates, m. p. 113°, whereas Winterstein, Vetter and Schön[5] subsequently

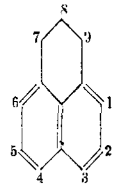
The synthesis of additional derivatives of known structure seemed to us of importance both for the purpose of exploring further the relationship between carcinogenic activity and structure and in order to provide reference substances for use in investigating the course of the oxidation,[6] diazo coupling,[11] and other substitutions[12] of the interesting hydrocarbon.[13] Because of the limitations in the succinic anhydride synthesis, a search was made for an alternate method of constructing the 3,4-benzpyrene ring system, and we can now report the development of a new synthesis which offers promise of considerable variation. An important step of the process involves a Scholl *peri*-condensation of a benzoylnaphthalene derivative, and in this respect the synthesis resembles that discussed but not tried by Cook and Hewett.[2] These authors expressed the view that 3,4-benzpyrene probably could be synthesized by application of the Scholl reaction to the benzoyl derivative of the ketone obtained by Mayer and Sieglitz[14] by the cyclization of β-(1-naphthyl)-propionic acid and regarded by them as having the structure I (for a discussion of the nomenclature of compounds I–III, see footnote[15]).



Perinaphthanone-7
I



Perinaphthenone
II



Perinaphthane
III

Cook and Hewett,[16] however, subsequently found that under certain conditions the cyclization gives a mixture of products, one of which is the unsaturated ketone II, apparently identical with the "pyrene ketone" obtained by Bamberger and Philip[17] in their degradation of pyrene.[17a] The English workers also observed in another connection that 4,5-benzhydrindone-3, a ketone somewhat analogous to I, failed to enter into a typical Friedel and Crafts reaction even at slightly elevated temperatures.[18] It was our plan to attempt to benzoylate not a ketone or diketone,[2] but the corresponding tricyclic hydrocarbon III.

peri-Trimethylenenaphthalene, for which we propose the new name perinaphthane,[15] was first isolated by Langstein,[19] who obtained a small amount of the crystalline hydrocarbon as a product of the degradation of pyrene. A synthesis was accomplished by Fleischer and Retze[20] from naphthalene and malonyl bromide, but the process involved reduction of the resulting diketone with hydrogen iodide and red phosphorus, followed by dehydrogenation of the over-reduced product, and the method is hardly practical for preparative purposes. In seeking a practical method we first considered the possibility of effecting a cyclization of 1-allylnaphthalene[21] into

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reported obtaining colorless needles, m. p. 135°, from methanol. In an effort to account for this discrepancy the earlier experiment in this Laboratory has been repeated (L. F. F.). A pure sample (6.3 g.) of 4′-keto-1′,2′,3′,4′-tetrahydro-3,4-benzpyrene (crystallized from dioxane[4]) was reduced by the Clemmensen method with added dioxane and toluene. The crude, twice distilled product (3.7 g., pale yellow, m. p. 110.5–112°) was crystallized repeatedly from glacial acetic acid and from alcohol, further purified by chromatographic adsorption (E. B. H.), and again crystallized from alcohol, when it formed lustrous, colorless plates, m. p. 112.6–113.1°, corr. This material appears to be a pure individual, and our earlier observation concerning the melting point of the product of Clemmensen reduction is thus confirmed. High pressure hydrogenation of the ketone was reported[3] to give low-melting crude material which affords pure 3,4-benzpyrene on dehydrogenation. We may now add that this crude product, although it appears to contain a considerable quantity of the above tetrahydride, is not homogeneous and probably consists of a mixture of hydro derivatives.

(11) Fieser and Campbell, THIS JOURNAL, **60**, 1142 (1938).

(12) Windaus and Rennhak, *Z. physiol. Chem.*, **249**, 256 (1937).

(13) Our hydrogenation, oxidation (lead tetraacetate), and reduction studies, THIS JOURNAL, **59**, 2331, 2502 (1937); **60**, 940 (1938), are also being extended to 3,4-benzpyrene.

(14) Mayer and Sieglitz, *Ber.*, **55**, 1835 (1922).

(15) *Note on Nomenclature.*—Cook and Hewett[16] have noted that three systems of naming these tricyclic compounds have been employed and that none of them is strictly correct. The ketone II has been referred to as pyrene ketone,[17] phenalone-9,[14,16] 1,8-naphthindenone[6] [see also Criegee, Kraft and Rank, *Ann.*, **507**, 177 (1933); Koelsch, THIS JOURNAL, **58**, 1326 (1936); Wojack, *Ber.*, **71**, 1102 (1938)], and *peri*-naphthindone.[25,26] While we hesitate to add to the confusion of the literature. there is as yet so little agreement or precedent that we venture to propose a system which seems to us more satisfactory than any heretofore employed. For the parent hydrocarbon with a saturated alicyclic bridge, the name *peri*-trimethylenenaphthalene is lengthy and not well adapted to naming *ac*-substitution products, "dihydrobenznaphthene" imputes to the unsaturated hydrocarbon "benznaphthene" [v. Braun and Rath, *ibid.*, **61**, 960 (1928)] a completely aromatic character which it does not possess, "dihydrophenalene" implies a closer relationship to benzene than to naphthalene, and "*peri*-naphthindane" suggests the presence of an indane system and a five-membered ring. The hydrocarbon has been made reasonably easily available in the present work and may assume a position of importance comparable with acenaphthene. The name suggested, perinaphthane, calls to mind significant features of the structure and can be modified to include various possible *ac*-derivatives by the usual conventions (compare cholestane). It does not represent a wide departure from at least one of the names prevously employed, for perinaphthane may be regarded as a condensation of *peri*-naphthindane. A lack of correspondence with parallel compounds of the acenaphthene (ace. from acetic) series is regrettable, but hardly avoidable, since the common name for the latter hydrocarbon does not conform to modern usage with respect to the alicyclic part of the molecule. It would have been more appropriate to use "acenaphthane" for the hydrocarbon with the saturated bridge and "acenaphthene" for its dehydro derivative.

(16) Cook and Hewett, *J. Chem. Soc.*, 365 (1934).

(17) Bamberger and Philip, *Ann.*, **240**, 178 (1887).

(17a) Professor Cook has called our attention to the more recent work of Darzens and Lévy, *Compt. rend.*, **201**, 902 (1935), who obtained a saturated ketone in excellent yield by conducting the cyclization in nitrobenzene solution.

(18) Cook and Hewett, *J. Chem. Soc.*, 1098 (1933).

(19) Langstein, *Monatsh.*, **31**, 867 (1910).

(20) Fleischer and Retze, *Ber.*, **55**, 3280 (1922).

(21) Tiffeneau and Daudel, *Compt. rend.*, **147**, 678 (1908).

the 8-position, but the only smooth transformation discovered gave a different result. When the substance was passed over alumina at 500–550° there was produced a liquid hydrocarbon corresponding in properties to α-propenylnaphthalene.[22]

We next investigated as a possible starting point for the preparation of the desired hydrocarbon in quantity a process described in the patent literature for the synthesis of the unsaturated ketone, perinaphthenone (II). According to an early patent[23] a yellow substance (m. p. 152°) of this probable structure can be obtained by heating either α- or β-naphthol with glycerol and 82% sulfuric acid, the acid presumably functioning as a dehydrating, condensing, and oxidizing agent. Cook and Hewett[16] noted that the reported properties are similar to those of Bamberger and Philip's[17] "pyrene ketone" (m. p. 142°) and of the product (m. p. 153–154°) formed with other substances from β-(1-naphthyl)-propionic acid under the cyclizing and dehydrogenating influence of stannic chloride[16] (or of aluminum chloride, acting on the acid chloride[14]). Finally Vollmann, *et al.*,[6] made a direct comparison of the material prepared according to the patent with a purified sample of "pyrene ketone" (m. p. 152°) and found the two to be identical. Although the original process did not seem very promising, a more recent patent[24] includes a detailed description of an improved procedure in which sodium nitrobenzene sulfonate is employed as the oxidizing agent. Silbermann and Barkow[25] have employed this procedure with success and have recorded further observations concerning the reaction. In our hands the reaction proceeded essentially as described in the patent. After finding a convenient method for recovering the product from the tarry reaction mixture, no difficulty was experienced in preparing the ketone in quantity (200 g.), and although the yield of pure product is only 26% of the theoretical, based on the β-naphthol used, the starting materials are of such a nature that this is not a very important consideration. Our purified perinaphthenone (II) melts at 156–156.5°, corr.

The only recorded attempt to reduce perinaphthenone is an experiment by Silbermann and Barkow[25] in which the ketone was treated with zinc and hydrochloric–acetic acid and the resulting oil distilled over zinc dust. This gave a very small amount of an evidently impure sample of perinaphthane (III). We investigated the hydrogenation of the ketone in the presence of Raney nickel, platinum oxide, and copper chromite catalyst with quite different results. With Raney nickel at atmospheric pressure the ketone in ether–alcohol absorbed 2 moles of hydrogen and gave as the chief product the previously unknown saturated alcohol, perinaphthanol-7. With Adams catalyst there was a rapid initial absorption of gas and a yellowish reaction product soon separated from the alcoholic solution. This substance is very sensitive and decomposes rapidly in solution. Rapid recrystallization gave deep yellow material for which analyses and molecular weight determinations suggest the structure of a dimolecular product of either reduction or reduction and condensation. This was not investigated further.

On hydrogenating the unsaturated ketone in dioxane or ether at high pressure in the presence of copper chromite catalyst we invariably obtained a mixture of the saturated alcohol and the hydrocarbon. As the temperature was increased less alcohol was found in the reaction mixtures, and it seems likely that the alcohol is produced in any case and, at the higher temperatures, is converted into perinaphthane by a process of dehydration and hydrogenation. It appeared, however, that the temperature cannot be increased beyond a certain point without offering opportunity for hydrogenation of the naphthalene nucleus. In order to avoid such over-hydrogenation and still maintain dehydrating conditions, the amount of catalyst was reduced to a minimum. Using but 2.5 mg. of catalyst per gram of ketone, it was found possible to conduct the hydrogenation at 250–260° in a reasonable time and obtain hydrocarbon of high purity in 70–74% yield.

With a satisfactory method available for the preparation of perinaphthane in quantity, little difficulty was experienced in completing the remaining steps of the 3,4-benzpyrene synthesis indicated in the chart. Benzoylation of the hydrocarbon by the Perrier method proceeded smoothly to give a crystalline product which we assume to be 3-benzoylperinaphthane (IV). For conversion into 2,1′-trimethylenebenzanthrone-10 (V) by the Scholl reaction it was found best to

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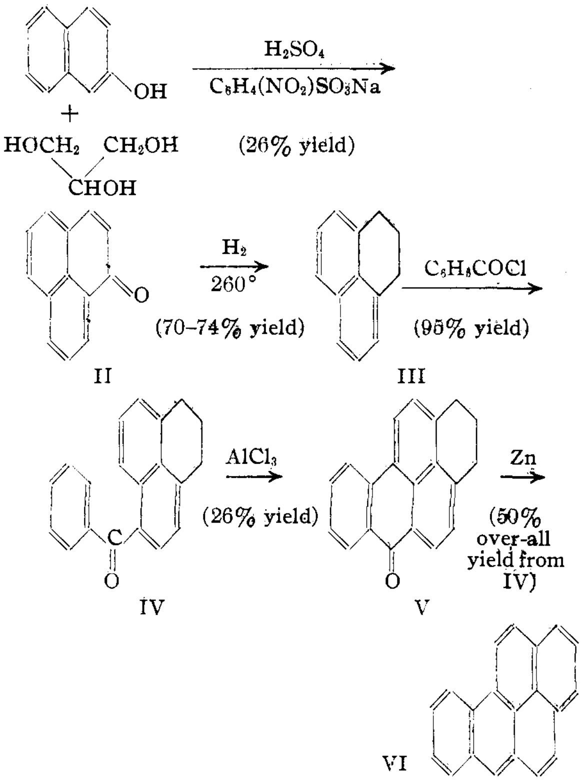
[22] Zal'kind and Zonis, *J. Gen. Chem.*, *U. S. S. R.*, **6**, 988 (1936).

[23] Bad. Anil. u. Sodafabrik, German Patent 283,066 (1915) [*Chem. Centr.*, **86**, I, 814 (1915)].

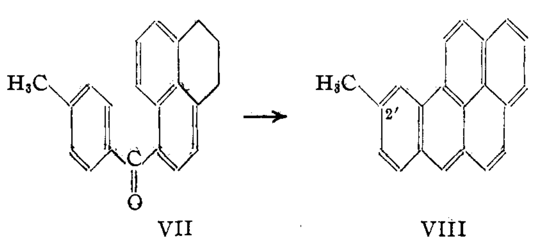
[24] I. G. Farbenindustrie, German Patent 614,940 (1935) [*C. A.*, **29**, 8009 (1935)].

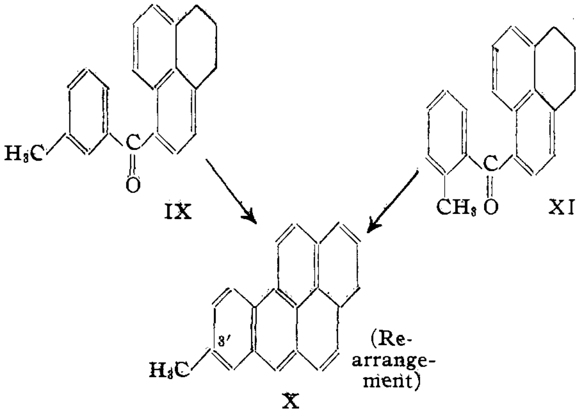
[25] Silbermann and Barkow, *J. Gen. Chem.*, *U. S. S. R.*, **12**, 1733 (1937).

heat the ketone IV in a sodium–aluminum chloride melt at 155° in an atmosphere of oxygen. A pure product was then isolated from the reaction mixture fairly readily, if in low yield, and on distillation with zinc dust it yielded pure 3,4-benzpyrene (VI). It was thought that hydro derivatives of V are probably formed in the Scholl reaction along with the benzanthrone derivative, and indeed the mother liquor material from V gave an additional quantity of 3,4-benzpyrene on zinc dust distillation. It was then found that the over-all yield of the hydrocarbon can be improved greatly by carrying out the cyclization process at a lower temperature without undue exposure to air and submitting the total amount of moist, gummy reaction product to distillation from a mixture with zinc dust. Conducted in this way, the synthesis affords 3,4-benzpyrene in over-all yield of 34% from perinaphthenone, or 9% from β-naphthol. The process is rapid and compares favorably with the older synthesis as a practical method of preparing the carcinogenic hydrocarbon.



In extending the synthesis, we investigated the three ketones resulting from the condensation of the isomeric toluyl chlorides with perinaphthane. The Scholl reaction was conducted under conditions judged from the above experience to give material best suited for conversion into the hydrocarbon rather than for the isolation of the benzanthrone derivatives, and these intermediates were not examined. The hydrocarbons did not prove difficult to purify, and the homogeneity was checked carefully by conversion to the beautifully crystalline, brilliant red trinitrobenzene complexes and recovery of the hydrocarbons by chromatographic adsorption of the trinitrobenzene on alumina from benzene solution. The *p*-toluyl compound VII gave in 42% yield a hydrocarbon which we regard as 2′-methyl-3,4-benzpyrene (VIII), m. p. 140–140.2°, corr. The *m*-toluyl ketone IX and the *o*-toluyl ketone XI gave, in 14 and 22% yield, an identical hydrocarbon, m. p. 147.6–148.1°. This compound is definitely different from the 2′-isomer, for both the hydrocarbon and its picrate give a distinct depression in melting point (the trinitrobenzene derivatives show no depression on admixture). There is reason to believe that the second hydrocarbon is 3′-methyl-3,4-benzpyrene (X), formed normally from the *m*-toluyl ketone and produced in the case of the *o*-toluyl ketone as the result of a migration of the methyl group to the adjacent position in the course of the Scholl reaction. If the *o*-toluyl ketone had reacted normally the hydrocarbon would be identical with the known 4′-methyl-3,4-benzpyrene,[8] m. p. 219.5–220°, corr.,[8] which is not the





case. Since there is little likelihood that both reactions proceed abnormally and still yield the same product, it is safe to assume that the ketone IX undergoes normal cyclization. Furthermore, the hydrocarbon in question corresponds fairly closely in melting point with the methylbenzpyrene (m. p. 143–144°, corr.) synthesized by Winterstein, Vetter and Schön[5] from pyrene and methyl succinic anhydride. This synthesis must give either the 2′- or 3′-isomer and, in analogy with known cases, the 3′-position is the more probable point of attachment. The correspondence between the substances obtained in two syntheses which would be expected to yield the 3′-isomer strengthens the belief that this structure is correct. Further support is derived from the analogy with the behavior of the three isomeric toluyl-α-naphthyl ketones. In extending earlier work, Fieser and Martin[26] proved that the meta and para isomers condense normally to the expected methylbenzanthrone, while the ortho compound gives the same product as the meta isomer, corresponding exactly to the conclusions reached above. The structures assigned in the present work therefore are open to little question.

A number of ramifications of the new synthesis are being investigated, and we can report now the isolation of two additional methylbenzpyrenes resulting from the addition of methyl lithium to the benzanthrone derivative V.

Experimental Part[27]

Isomerization of α-Allylnaphthalene.—For preparation of the hydrocarbon,[21] the Grignard reagent from 207 g. of α-bromonaphthalene and 36 g. of magnesium in ether (600 cc.)–benzene was added in two hours, with stirring under reflux, to 121 g. of allyl bromide in 250 cc. of benzene. After refluxing further for two and one-half hours, the hydrocarbon fraction was separated and distilled, b. p. 220–235° (8 mm.); yield, 154 g. (92%). Fractionation through a 1-meter column gave 137 g. (81%) of material, b. p. 127.5–128.5° (8 mm.), n^{25}D 1.6089.

The picrate, obtained from a cold, concentrated methanol solution, formed orange needles, m. p. 68–69°.

Anal. Calcd. for $C_{13}H_{12}\cdot C_6H_3O_7N_3$: N, 10.59. Found: N, 11.00.

Fifteen grams of α-allylnaphthalene was distilled slowly through a tube of activated alumina at 500–550° at a pressure of 15 mm. The condensate consisted of a light yellow oil, b. p. 125–135° (8 mm.). Treated in alcoholic solution with two successive 5-g. portions of picric acid, the oil yielded 7.9 g. of picrate, m. p. 109–110°, and 6.2 g., m. p. 106–108°. Crystallized to constant melting point, the picrate formed orange needles, m. p. 110–111°.

Anal. Calcd. for $C_{13}H_{12}\cdot C_6H_3O_7N_3$: N, 10.59. Found: N, 10.99.

The hydrocarbon was recovered from the purified picrate by adsorption of the nitro compound on alumina from benzene and obtained as a yellow oil (4.9 g.), b. p. 139–140° (10 mm.), n^{20}D 1.6350. The constants given by Zal'kind and Zonis[22] for α-propenylnaphthalene are b. p. 105–106° (6 mm.), n^{20}D 1.6388. On oxidation of the hydrocarbon with sodium dichromate there was a strong odor of acetaldehyde and α-naphthoic acid, m. p. 158–159°, was isolated in good yield.

Perinaphthenone (II).—For the preparation of a quantity of the ketone the condensation was run conveniently in three lots, which were then combined for recovery of the product. In each lot the charge consisted of 460 cc. of water, 675 cc. of concentrated sulfuric acid, 250 g. of technical sodium nitrobenzene sulfonate, 500 g. of glycerol and 200 g. of β-naphthol. The reagents were mixed in this order in a 3-liter three-necked flask provided with a short condenser in the center opening, a mechanical stirrer (tantalum wire stirrer) working through the condenser, and a thermometer. The mixture was stirred and heated cautiously as required to maintain a temperature of 130–140° for one hour. (The reaction is exothermic and is apt to get out of control if a heating bath is used.) The dark solution was decanted while hot from a tarry residue through a pad of glass wool in a funnel onto 2–3 liters of ice in a series of beakers. After dilution to a total volume of about 6 liters, the mixtures were kept at 0° for one or two hours to allow the precipitated tar to agglomerate and the supernatant liquor was then decanted and discarded. The next two lots of reaction mixture were poured in succession onto ice in the same beakers, discarding the acid liquor and retaining the tar. The total tar, which becomes soft and mobile when warm, was then extracted with six 1-liter portions of benzene, heating the mixture on the hot-plate with mechanical stirring. The decanted extracts were filtered, combined, clarified with decolorizing carbon, and concentrated. After removing the solvent the product was distilled in vacuum, and there was obtained 209 g. of orange-yellow distillate boiling at 190–200° at 1–3 mm. For crystallization this was dissolved in 500 cc. of benzene and 500 cc. of ligroin (b. p. 80–86°) was added at the boiling point. This crystallization gave 196 g. (26%) of product in the form of yellow prisms, m. p. 154.5–155.5°. A sample recrystallized from benzene–ligroin formed elongated, diamond-shaped prisms, m. p. 156–156.5°.

The tar remaining from the benzene extraction dissolves fairly readily in hot water. The proportion of glycerol specified is considerably greater than that specified in the patent[24] and by Silbermann and Barkow,[25] for it was our experience in trial runs that this modification results in a definitely superior product. No advantage was found in increasing the proportion still further. Slow addition of the β-naphthol, as specified by Silbermann and Barkow, did not improve the result, nor did changes in the proportion of the oxidizing agent. In one trial with α-naphthol the yield was not as good as with the β-isomer.

Perinaphthane (III).—In the procedure found most satisfactory the charge consisted of 20 g. of perinaph-

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(26) Fieser and Martin, THIS JOURNAL, **58**, 1443 (1936).

(27) All melting points are corrected. Microanalyses by the Arlington Laboratories, Arlington, Virginia.

thenone, 25 cc. of peroxide-free dioxane, and 50 mg. of copper chromite catalyst 37 KAF. This was placed in the bomb in a glass liner and hydrogenation was conducted at an initial pressure of 1800 lb. (120 atm.) and a temperature of 250–260° for ten hours. On cooling, the solution separated into two layers and dioxane was added to make it homogeneous. After filtering from the catalyst the solvent was removed in vacuum and the product distilled at 8 mm. pressure. The fraction boiling at 140–165° (15.8 g.) consisted largely of the desired hydrocarbon, and the remaining distillate, b. p. 165–190°, was mainly perinaphthanol (see below).

Crystallization of the hydrocarbon fraction from 50–75 cc. of methanol diluted with a few cubic centimeters of water gave 11.7 g. (m. p. 63.5–64.5°) of perinaphthane in the first crop and 1.3 g. (m. p. 62–63°) in the second; total yield 70%. In a duplicate experiment the yield was 74%.

In pilot experiments hydrogenation was tried at temperatures below 200° with ether as solvent and without a solvent, but the yield of hydrocarbon was never better than 45%. It seems advantageous to use a solvent for there is then less gum left as a residue from the distillation. Yields of 45–58% were obtained in 20-g. runs at 200–230° using from 100 to 750 mg. of catalyst, and it was noticed that the use of a large amount of catalyst tended to give material of inferior melting point, possibly because of over-hydrogenation. This suggested the use of a very small quantity of catalyst, a higher temperature, and a pressure as low as possible, as specified in the procedure given above.

Further purification of perinaphthane by repeated crystallization from dilute methanol gave thin, colorless plates of the constant melting point 65.1–65.4°. We cannot confirm the melting point 68–69° reported by Langstein,[19] or 66–67° given by Fleischer and Retze.[20] Our hydro carbon, like Langstein's, darkens on exposure to light.

The picrate forms fine orange-red needles from methanol and melts at 150–151°.

Anal. Calcd. for $C_{13}H_{12}\cdot C_6H_3O_7N_3$: N, 10.58. Found: N, 10.62.

It is doubtful whether previous investigators had the pure substance in hand, for melting points of 127° (Langstein[19]), 134–135° (Fleischer and Retze[20]), and 132–133° (Silbermann and Barkow[25]) are given, all with previous darkening.

The trinitrobenzene derivative formed long, yellow needles from methanol and melted at 160–161°, in agreement with the value 159–160° reported by Fleischer and Retze.[20]

Perinaphthanol-7.—This alcohol, formed in varying amounts in the above experiments, was obtained as the chief product of hydrogenation under the following conditions. A solution of 5 g. of perinaphthenone in 100 cc. of ether (distilled from a Grignard solution) and 25 cc. of absolute alcohol was shaken with hydrogen at atmospheric pressure in the presence of 0.5 g. of Raney nickel. There was a transient deep brown color at the start and the absorption of gas reached 2 moles in about five hours. After filtering from the catalyst and removing the solvent there was obtained on distillation in vacuum 3.2 g. of pale yellow distillate, b. p. 158–161° (1 mm.), and 0.9 g. of deep red distillate, b. p. 161–200° (1 mm.); considerable tar was left in the flask. The first fraction (solid) on crystallization from ligroin (b. p. 80–86°) gave 2.5 g. (49%) of colorless, crystalline product, m. p. 81–85°. After six further crystallizations the material formed glistening blades, m. p. 91.5–93°, and the picrate formed dull orange needles, m. p. 159–160°, from benzene–ligroin. This sample of the alcohol appears to be less satisfactory than those described below, and the substance seems to be very difficult to purify.

Crystallization from ligroin of the high-boiling fraction from the high-pressure hydrogenation gave a sample of the alcohol melting at 100.5–101.5° and showing no depression when mixed with the lower melting material. The picrate in this case melted at 163–165°. Surprisingly enough, the best sample was obtained from material recovered from an attempted dehydration. One gram of crude alcohol, m. p. 81–85°, was heated with a little potassium bisulfate at 180–200° for five minutes and the product distilled at 10 mm. pressure. There was considerable tarry residue, and the light yellow distillate afforded only 0.25 g. of crude, crystalline product from ligroin (b. p. 60–70°). After six recrystallizations, the sample melted at 105.5–106°. This sample was analyzed.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.96; H, 6.38.

The picrate, prepared from the best sample and crystallized from benzene–ligroin, formed fine, dull orange needles, m. p. 163.5–164.5°.

Anal. Calcd. for $C_{13}H_{12}O\cdot C_6H_3O_7N_3$: N, 10.14. Found: N, 9.92.

Hydrogenation with Adams Catalyst.—A solution of 2 g. of perinaphthenone in 40 cc. of absolute alcohol with 30 mg. of platinum oxide catalyst quickly turned deep brown when shaken with hydrogen at slight positive pressure, and after a few minutes a yellowish solid began to precipitate. (The behavior was the same when a small amount of hydrochloric acid was added to the alcoholic solution.) After the absorption of 1 mole of gas (several hours), the solid was collected with the adhering catalyst and washed with dry ether (weight 1.75 g.). The material was dissolved in 40 cc. of hot dioxane and the solution was quickly filtered and diluted with 50 cc. of hot water. The first crop of crystals (0.25 g) formed small, orange-yellow needles, m. p. 179–180°, dec. The substance decomposes rapidly in solution and recrystallization usually gives inferior material and is attended with heavy losses. Decomposition was evident in an attempted molecular weight determination in camphor.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.78; H, 5.54; mol. wt., 364. Calcd. for $C_{26}H_{18}O_2$: C, 86.18; H, 5.01; mol. wt., 362. Found: C, 86.06, 85.81; H, 5.41, 5.59; mol. wt. (ebullioscopic in acetone), 320, 348.

3-Benzoylperinaphthane (IV).—The Perrier complex from 45 g. of benzoyl chloride and 43.3 g. of aluminum chloride was dissolved in 500 cc. of carbon bisulfide and added with shaking to 52 g. of perinaphthane in 150 cc. of the same solvent. The clear, deep red solution was refluxed for one-half hour and decomposed with ice and acid. After evaporation of the solvent the oily product was extracted and washed in ether and distilled, giving 79.9 g.

(95%) of material, b. p. 210–215° (2 mm.) which slowly solidified. This was suitable for use in the next step. A sample recrystallized twice from ether–petroleum ether formed massive, faintly cream-colored prisms melting at 62–63°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.21; H, 5.92. Found: C, 87.96; H, 5.95.

2,1′-Trimethylene-1,9-benzanthrone-10 (V).—The most satisfactory procedure found for preparing this intermediate, rather than utilize it in the synthesis, was as follows. A melt was prepared from 23 g. of sodium chloride and 80 g. of aluminum chloride, and 19.6 g. of benzoylperinaphthane was added. The mixture was heated for four hours in a bath maintained at 150–155°, while stirring mechanically and passing oxygen over the surface of the melt. The hot melt was then poured onto ice and hydrochloric acid and the brown, gummy precipitate was collected and taken into glacial acetic acid while still wet. Four crystallizations from this solvent, with the liberal use of decolorizing carbon each time, gave in all 5.0 g. (26%) of iridescent golden-yellow leaflets, m. p. 217–218°. The substance is readily soluble in benzene, rather sparingly soluble in glacial acetic acid, and only slightly soluble in alcohol. In very dilute alcoholic solution it exhibits a striking yellow-green fluorescence. The solution in concentrated sulfuric acid shows a brilliant red-yellow fluorescence.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 89.05; H, 5.24.

The material precipitated from the mother liquors of the above experiment by dilution with water was distilled with zinc dust as described below and yielded 2.2 g. (12%) of 3,4-benzpyrene. A small sample of the pure benzanthrone derivative was converted in the same way into the hydrocarbon.

3,4-Benzpyrene.—A melt was prepared from 23 g. of sodium chloride and 80 g. of aluminum chloride in a 125-cc. Erlenmeyer flask, 15.1 g. of 3-benzoylperinaphthane was added, and the flask was stoppered loosely and heated with occasional shaking in an oil-bath held for three hours at 130–140° and for two hours longer at 145–150°. The ketone dissolves readily in the melt giving at the outset a deep red solution which turns brown as the reaction proceeds. At the end of the time specified this was poured onto ice and acid and the gummy precipitate was collected on a filter, washed with water, and sucked well. The crude, moist material, which darkens appreciably during the washing, was shredded and mixed with 250 cc. of zinc dust in a 300-cc. round-bottomed flask sealed direcily to a distilling flask with a sealed-on receiver. The distillation was conducted from a sodium–potassium nitrate bath at a dull red heat and was continued as long as distillate collected in the distilling flask (one-half to one hour). The crude product was then distilled into the second receiver at a pressure of 1–2 mm. This eliminated entrained zinc dust and a tarry residue and gave a clean distillate easily purified by dissolving it in ether, concentrating, and adding successive portions of petroleum ether until crystallization was complete. The first crop (5.8 g.) consisted of light yellow needles, m. p. 176–177°, and the second (1.2 g.) melted at 172–175°; total yield, 50%. When the zinc dust distillation was conducted at too low a temperature, or too rapidly, the product often crystallized in the form of leaflets of lower melting point; this probably is due to contamination with hydro derivatives. When the Scholl reaction was conducted with stirring in the presence of oxygen as above and the crude product put through the zinc dust distillation the yield of hydrocarbon was about half that obtained by the process described.

The hydrocarbon was fully identified by comparison with known material.[3] For further characterization, and for comparison with the new derivatives described below, the hitherto unknown **3,4-benzpyrene–trinitrobenzene** was prepared. It formed glistening, bright red blades from benzene, m. p. 226–227°.

Anal. Calcd. for $C_{20}H_{12} \cdot C_6H_3O_6$: N, 9.03. Found: N, 9.00.

Unlike the corresponding complex from methylcholanthrene,[28] this trinitrobenzene derivative can be cleaved effectively with full recovery of the hydrocarbon by selective adsorption of the nitro component on alumina from benzene solution. The recovered hydrocarbon after crystallization melted at 178.5–179°.

The Isomeric 3-Toluylperinaphthanes.—These were prepared as above from the reaction of the Perrier complex of the appropriate toluyl chloride and perinaphthane (from 8 to 13 g.) in carbon bisulfide solution, distilled in vacuum for use in the syntheses, and crystallized for analysis from ether–petroleum ether or from ether. The properties and yields are given in the table. They all form massive prismatic clusters and were obtained in either a colorless or pale yellow condition.

TABLE I

o-, *m*- AND *p*-TOLUYLPERINAPHTHANE ($C_{21}H_{18}O$)

					Analyses	
Isomer	M. p., °C.	B. p., °C.	Mm.	Yield, %	% C (Calcd. 88.06)	% H (Calcd. 6.33
Ortho	68–69	210–215	0.2	84	87.83	6.41
Meta	86.5–87	225–230	2	95	88.13	6.42
Para	90–90.5	215–220	0.5	95	88.13	6.29

2′-Methyl-3,4-benzpyrene (VIII).—A solution of 16.9 g. of 3-(*p*-toluyl)-perinaphthane in a melt from 23 g. of sodium chloride and 80 g. of aluminum chloride was heated in a stoppered flask at 140–150° for four and one-half hours. The crude, moist product was mixed with 150 cc. of zinc dust and distilled slowly as before, except that the pressure was reduced to 200–250 mm. to allow for a higher boiling point of the methylated hydrocarbon. Crystallization of the distillate gave in all 6.8 g. (42%) of material melting in the range 130–136°. This was converted into the trinitrobenzene complex, which was crystallized to a constant melting point of 212–213° and then passed in benzene solution through an adsorption tower of alumina. The regenerated hydrocarbon collected from the filtrate was crystallized once from benzene–ligroin and three times from methanol. It forms fluffy, light yellow needles and has a double melting point. When heated slowly it melts almost completely at 138–139°, and after solidification by cooling it remelts at 140–140.2°. It is readily soluble in benzene and ether, moderately soluble in metha-

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(28) Fieser and Hershberg, THIS JOURNAL, **60**, 940 (1938).

nol, and almost insoluble in petroleum ether. The solubility is greater than that of the parent hydrocarbon.

Anal. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.85; H, 5.51.

The **trinitrobenzene complex** forms glistening red blades from benzene–ligroin, m. p. 211.5–212°.

Anal. Calcd. for $C_{21}H_{14}\cdot C_6H_3O_6N_3$: N, 8.77. Found: N, 8.95.

The **picrate** forms brown needles from benzene–ligroin, m. p. 184–185°.

Anal. Calcd. for $C_{21}H_{14}\cdot C_6H_3O_7N_3$: N, 8.48. Found: N, 8.35.

3′-Methyl-3,4-benzpyrene (X). (a) Normal Reaction.—3-(*m*-Toluyl)-perinaphthane (9.4 g.) was heated with sodium–aluminum chloride in a closed flask at 135–150° for four and one-half hours and the product distilled from zinc dust at atmospheric pressure. The once crystallized distillate melted at 138–142°; yield, 1.3 g. (14%). A benzene solution of this material was passed through a tower of alumina and the recovered product was crystallized six times from ether–ligroin and ether–absolute alcohol. This gave small, faintly greenish-yellow needles. The hydrocarbon apparently exists in two forms of slightly different melting point. When heated slowly the sample melted at 146.5–147°, but when inserted in a bath at 145° it melted at once. The resolidified material melts at 147.6–148.1°. The melting point and appearance remained unchanged on further passage through an adsorption tower and on regeneration from the purified trinitrobenzene derivative. The hydrocarbon is somewhat less soluble than the 2′-isomer.

Anal. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.52; H, 5.04.

The trinitrobenzene complex forms long, brilliant red needles from benzene–ligroin, m. p. 210.5–211°.

Anal. Calcd. for $C_{21}H_{14}\cdot C_6H_3O_6N_3$: N, 8.77. Found: N, 8.55.

The picrate separated from benzene–ligroin as fine brownish-red needles, m. p. 179.5–180°.

Anal. Calcd. for $C_{21}H_{14}\cdot C_6H_3O_7N_3$: N, 8.48. Found: N, 8.42.

Mixtures of the hydrocarbon with the 2′-isomer were found to melt as low as 123–128°, and a depression to 171–173° was noted with a mixture of the two picrates. The trinitrobenzene derivatives melt at practically identical temperatures and no depression was observed with mixtures.

(b) By Rearrangement.—The Scholl reaction was conducted as above with 12 g. of 3-(*o*-toluyl)-perinaphthane (four hours at 150–160°) and the distillation from zinc dust carried out at 100–200 mm. pressure. The redistilled and once crystallized product formed straw-yellow needles, m. p. 143–145°; yield, 2.6 g. (22%). After further crystallization from ether–petroleum ether it melted at 146.5–147.5° and gave no depression when mixed with the first sample (a). The melting points and mixed melting points of the picric acid and trinitrobenzene complexes were also identical with those of the above samples.

Summary

The first step in the synthesis consists in condensing β-naphthol with glycerol essentially as described in a patent. The resulting unsaturated ketone, for which the name perinaphthenone is proposed, can be reduced satisfactorily to the hydrocarbon (perinaphthane, in the suggested system of nomenclature) by high pressure hydrogenation. The benzoyl derivative of the hydrocarbon undergoes the Scholl cyclization fairly smoothly, and 3,4-benzpyrene is obtained in good over-all yield by zinc dust distillation of the product.

Of the isomeric toluyl derivatives of perinaphthane, the meta and para compounds undergo normal cyclization and give as final products of the synthesis 3′- and 2′-methyl-3,4-benzpyrene, respectively, while with the ortho isomer there is methyl migration leading to the ultimate formation of 3′-methyl-3,4-benzpyrene. These results parallel those obtained in the application of the Scholl reaction to the preparation of the corresponding methylbenzanthrones.

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