

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## 9-Methyl-3,4-benzpyrene

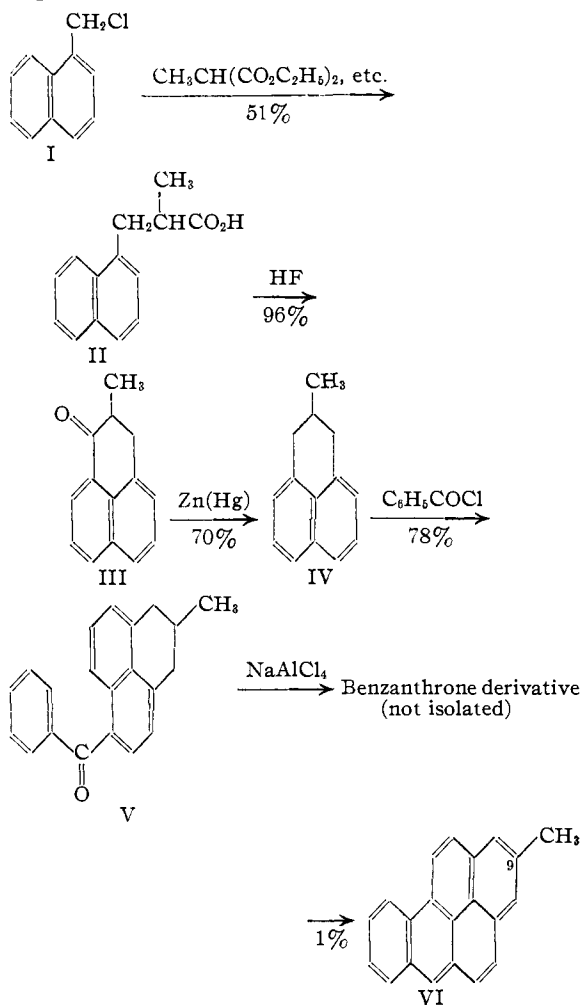
BY LOUIS F. FIESER AND FREDERICK C. NOVELLO

Of the twelve possible monomethyl derivatives of 3,4-benzpyrene the 2'-,<sup>1</sup> 3'-,<sup>1,2</sup> 4'-,<sup>3</sup> 5-<sup>4</sup> and 6-<sup>4</sup> isomers have been synthesized and submitted to tests for carcinogenic activity. This paper reports the synthesis of a sixth isomer, having the substituent at the 9-position.

The previously described route through a perinaphthene derivative<sup>1</sup> was selected as offering the most promising approach to the desired hydrocarbon, and the required intermediate was synthesized satisfactorily as follows.  $\alpha$ -Chloromethyl-naphthalene (I), prepared readily by Cambron's

procedure<sup>5</sup> in 45% yield, was converted in good yield with the use of methyl malonic ester into  $\beta$ -(1-naphthyl)-isobutyric acid (II). Cyclization of this acid (m. p. 92°) proceeded very smoothly under the influence of hydrogen fluoride, giving a liquid ketone of narrow boiling range. The homogeneity of the material is indicated by the ready formation of a sharply melting, if heat sensitive, oxime, and the direction of ring closure follows from the conversion of the ketone to 1,8-naphthalic acid by oxidation. The substance therefore is 8-methylperinaphthanone-7 (III). The Clemmensen reduction proceeded most satisfactorily when conducted in a benzene-methanol mixture<sup>6</sup> with avoidance of too prolonged heating and with careful exclusion of light. With adequate precautions in the preparation and purification, 8-methylperinaphthene (IV) can be obtained by distillation in a nitrogen atmosphere as a nearly colorless, mobile oil, but it is highly sensitive to light, heat and air and on exposure it rapidly acquires a deep orange color. The exposed material gave no test for peroxide with magnesium phthalocyanine dihydride<sup>7</sup> but left a considerable residue on redistillation. The liquid hydrocarbon can be identified as the trinitrobenzene derivative, m. p. 149-150°.

Interaction of the hydrocarbon with the benzoyl chloride Perrier-complex at 0° gave a ketone which distilled as a viscous oil affording a crystalline trinitrobenzene derivative. In view of the orientation established for perinaphthene,<sup>8</sup> this can safely be assumed to be the 3-benzoyl derivative V. The Scholl ring closure with sodium aluminum chloride was tried under a variety of conditions but proceeded less successfully than in the instances reported<sup>1</sup> and a crystalline benzanthrone derivative could not be isolated. Zinc dust distillation of the total tarry reaction product gave mixtures which, after considerable processing through the trinitrobenzene complex and by chromatographic adsorption, afforded small amounts of an apparently homogeneous hydrocarbon having the com-

(1) Fieser and Hershberg, *THIS JOURNAL*, **60**, 1658 (1938).(2) Winterstein, Vetter and Schön, *Ber.*, **68**, 1079 (1935).(3) Fieser and Fieser, *THIS JOURNAL*, **57**, 782 (1935).(4) Fieser and Hershberg, *ibid.*, **60**, 2542 (1938).(5) Cambron, *Can. J. Research*, **17B**, 10 (1939).(6) Fieser, Fry and Jones, *THIS JOURNAL*, **61**, 1849 (1939); Fieser, Campbell, Fry and Gates, *ibid.*, **61**, 3218 (1939).(7) Helberger, Rebay and Fettback, *Ber.*, **72**, 1643 (1939).(8) Fieser and Hershberg, *THIS JOURNAL*, **62**, 49 (1940).

position of 9-methyl-3,4-benzpyrene (VI). This usually was accompanied by the higher melting and less soluble 3,4-benzpyrene, particularly when a high temperature was maintained in the distillation. At a lower temperature the only crystalline material found present along with VI was low melting and appeared to be a mixture of hydrides. The solubility and crystalline character of 9-methyl-3,4-benzpyrene were such as to make possible the separation of the substance in a condition of high purity and sharp melting point. The hydrocarbon melts at 147.2–148°, corr., and gives a bright red trinitrobenzene derivative, m. p. 218.5–219.5°. It is interesting that the melting points of the other five methylbenzpyrenes range from 140 to 220°, while the trinitrobenzenes melt from 210 to 231°. The new hydrocarbon clearly is different from the substance, m. p. 171–172.5°, obtained by Bergmann and Blum-Bergmann<sup>9</sup> and regarded as a methyl-3,4-benzpyrene,<sup>10</sup> possibly with the substituent in the 9-position.<sup>11</sup> The structure of our hydrocarbon, to be sure, is subject to some uncertainty because of the low yields in the last two steps of the synthesis.

The results of various exploratory experiments in the pyrene series have been included in this report. In the synthesis of 3,4-benzpyrene the yield of the intermediate ketotetrahydride was raised to 95% by using phosphorus pentachloride for the preparation of the acid chloride<sup>12</sup> and stannic chloride to effect cyclization.<sup>3,13</sup> The ozonization of 3,4-benzpyrene was studied, but the material appeared either to remain unchanged or to be attacked extensively, and no satisfactory products were isolated. Ozonization procedures were used which had been tested by their successful application to pyrene. Vollmann and co-workers<sup>12</sup> obtained phenanthrene-4-aldehyde-5-carboxylic acid in fair yield by ozonizing the hydrocarbon in acetic acid and effecting decomposition with water and alkali. On prolonged ozonization they obtained biphenyl-2,2',6,6'-tetracarboxylic acid. We obtained similar results by this procedure but found it more satisfactory to decompose the ozonide by catalytic hydrogenation.<sup>14</sup> The initial product by this method was

(9) E. Bergmann and Blum-Bergmann, *THIS JOURNAL*, **58**, 1678 *ibid.*, (1936).

(10) Hewett, *J. Chem. Soc.*, 193 (1938).

(11) E. Bergmann and F. Bergmann, *THIS JOURNAL*, **60**, 1805 (1938).

(12) Vollmann, Becker, Corell and Streeck, *Ann.*, **531**, 1 (1937).

(13) Fieser, Hershberg, Long and Newman, *THIS JOURNAL*, **59**, 475 (1937).

(14) F. G. Fischer, Düll and Ertel, *Ber.*, **65**, 1467 (1932).

again the 4-aldehyde-5-acid, even after brief periods of ozonization in experiments conducted in ethyl acetate, ethyl chloride or anhydrous pyridine in the hope of isolating the dialdehyde. Prolonged ozonization, followed by catalytic decomposition of the ozonide, gave mixtures from which we isolated crystalline substances which from the analyses appear to be biphenyl-2,2',6,6'-tetraldehyde and the corresponding 2,2',6,6'-tetrahydroxymethyl compound.

Since pyrene is attacked preferentially by ozone at the 1,2,6- and 7-positions, it seemed possible that the symmetrical tetrahydride might be obtainable in practical quantity by hydrogenation under conditions less drastic than employed by Coulson.<sup>15</sup> It was found that in the presence of copper chromite catalyst the completely sulfur-free hydrocarbon could be hydrogenated rapidly at temperatures as low as 108°, but the chief product was the *s*-hexahydride.<sup>16</sup>

### Experimental Part<sup>17</sup>

**Starting Materials.**— $\alpha$ -Chloromethylnaphthalene was prepared according to Cambron<sup>5</sup> except that the mixture was stirred mechanically. The yield from 288 g. of naphthalene after a reaction period of four and one-half hours was 214 g. (54%), b. p. 120–140° at 1 mm. A redistilled fraction, b. p. 120–125°, was used in the synthesis.

Ethyl methylmalonate was prepared by a procedure worked out by Dr. Nathan Weiner and outlined below with his permission.<sup>18</sup> In a flask previously baked out while sweeping with nitrogen, 47 g. of sodium was added in portions under nitrogen to 700 cc. of commercial absolute alcohol. When solution was complete (four hours) 320 g. of malonic ester was added with stirring during one-half hour, and then methyl bromide generated according to Lucas and Young<sup>19</sup> was passed in to the point of saturation (four hours). After refluxing until the mixture was neutral to litmus (one and one-half hours) about half of the alcohol was distilled off under vigorous stirring. The mixture was cooled, the sodium bromide was collected by filtration and saved, and the filtrate concentrated to about 200 cc. and poured into 800 cc. of water and 40 cc. of concentrated hydrochloric acid. The aqueous layer which separated was extracted with 600 cc. of ether in three portions and the combined organic fractions were washed with a saturated aqueous solution (in three portions) of the above sodium bromide precipitate. After removal of the solvent the residual oil was cooled and shaken for two minutes with a solution of 12 g. of potassium hydroxide in 36 cc. of water to remove any ethyl malonate. After washing with dilute acid and water the solution was dried

(15) Coulson, *J. Chem. Soc.*, 1298 (1937).

(16) Cook and Hewett, *ibid.*, 404 (1933).

(17) All melting points are corrected.

(18) The detailed procedure, which is based in part upon observations of Michael, *J. prakt. Chem.*, **72**, 537 (1905); and Salkowski, *ibid.*, **106**, 255 (1923), has been submitted to "Organic Syntheses."

(19) Lucas and Young, *THIS JOURNAL*, **51**, 2535 (1929).

and concentrated and the ethyl methylmalonate was distilled; b. p. 85–87° at 11–12 mm., yield 307 g. (88%).

**$\beta$ -(1-Naphthyl)-isobutyric Acid (II).**—A solution prepared from 26.5 g. of sodium and 400 cc. of absolute alcohol was stirred under reflux and treated with 174 g. of ethyl methylmalonate, added during one-half hour. After stirring for one hour further, a solution of 176.5 g. of  $\alpha$ -chloromethylnaphthalene in 50 cc. of absolute alcohol was added over a period of one hour (exothermic reaction). After refluxing for two hours and stirring for an equal period without heating, about 200 cc. of alcohol was distilled and the cooled residue was poured into 700 cc. of water containing 200 cc. of concentrated hydrochloric acid. The mixture was extracted thoroughly with ether and the solution washed with soda, acid and water, dried and evaporated. The malonic ester derivative distilled as a faintly yellow, viscous oil, b. p. 175–176° at 1 mm., yield 221 g. (70.5%).

A solution of this ester in 150 cc. of 95% alcohol was refluxed for two hours with 84 g. of potassium hydroxide in 500 cc. of water. The clear solution was cooled, diluted with 500 cc. of water and extracted with ether. The alkaline layer was acidified and the resulting oil was collected and washed in ether and the crude acid heated in an oil-bath at 180–185° for one-half hour to effect decarboxylation. The viscous oil was taken up in hexane, from which the acid II separated on cooling in clusters of colorless needles, m. p. 91.8–92.6°; yield 110 g. (73%).

*Anal.* Calcd. for  $C_{14}H_{14}O_2$ : C, 78.48; H, 6.59. Found: C, 78.83; H, 6.79.

**8-Methylperinaphthanone-7 (III).**—A solution of 10 g. of  $\beta$ -(1-naphthyl)-isobutyric acid in 165 g. of anhydrous hydrogen fluoride was allowed to stand at room temperature for two hours and poured onto ice. The precipitated yellow oil was taken up in ether, and, after washing and drying, the product was obtained by distillation as a mobile, yellow oil, b. p. 135–136° at 0.5 mm.; yield 8.8 g. (96%).

*Anal.* Calcd. for  $C_{13}H_{12}O$ : C, 85.68; H, 6.17. Found: C, 85.46; H, 6.21.

To establish the structure, 1 g. of the ketone was oxidized with sodium dichromate (7.5 g.) in glacial acetic acid (25 cc.). The product, precipitated with water and crystallized from alcohol, formed colorless needles, m. p. 273–274°, and gave no depression when mixed with authentic naphthalic acid.

For further characterization a sample of the ketone was converted to the oxime, which crystallized from dilute alcohol in the form of colorless needles, m. p. 147.2–148.2°. The substance is sensitive to heat, for some darkening occurred on drying in vacuum at 100° and after a few weeks the sample had decomposed to a black oil.

*Anal.* Calcd. for  $C_{14}H_{13}ON$ : C, 79.59; H, 6.20. Found: C, 79.72; H, 6.07.

**8-Methylperinaphthane (IV).**—After several trials it was found best to use a modified Clemmensen reduction procedure<sup>6</sup> and to conduct the reaction in a flask wrapped with asbestos in order to protect the hydrocarbon from the action of light. A mixture of 13 g. of the ketone, 50 g. of amalgamated mossy zinc, 125 cc. of methanol, 125 cc. of benzene, and 30 cc. of concentrated hydrochloric acid

was boiled under reflux for eight to nine hours (no longer) with the addition of 25 cc. of fresh acid in two portions. After cooling, separating the layers, and extracting the aqueous layer with ether, the product was collected and distilled under nitrogen. The hydrocarbon came over as a mobile, faintly lemon-yellow oil, b. p. 135° at 1.5 mm.; yield 8.5 g. (70%).

*Anal.* Calcd. for  $C_{14}H_{14}$ : C, 92.26; H, 7.74. Found: C, 92.20; H, 7.79.

The hydrocarbon formed a trinitrobenzene derivative which after four crystallizations from benzene–ligroin formed glistening reddish-brown needles, m. p. 149–150°, dec. The marked sensitivity of the hydrocarbon, particularly to air and light, has been mentioned above. In some runs, the product was distinctly yellow even after distillation in nitrogen and a second careful distillation was required to give practically colorless material. A sample exposed to sunlight became deep orange within two hours.

**3-Benzoyl-8-methylperinaphthane (V).**—The Perrier complex prepared from 2.67 g. of aluminum chloride and 2.81 g. of benzoyl chloride was dissolved in 75 cc. of carbon bisulfide and added in about ten minutes to a solution of 3 g. of 8-methylperinaphthane in 50 cc. of carbon bisulfide at 0°. After standing with occasional shaking at 0° for forty-five minutes, the deep red solution was poured onto ice and acid and the solvent was removed by heating on the steam-bath. The resulting dark red oil was extracted with ether and the solution was washed with alkali until no pink coloration appeared in the washings, and then with water. After drying and removing the solvent, the product distilled (under nitrogen) as a very viscous, amber colored oil, b. p. 215–220° (2 mm.); yield 3.7 g. (78%). When yellow colored methylperinaphthane was used the yield was 10–15% lower.

*Anal.* Calcd. for  $C_{21}H_{18}O$ : C, 88.07; H, 6.34. Found: C, 87.94; H, 6.41.

The trinitrobenzene derivative crystallized from benzene–ligroin as golden-yellow needles, m. p. 107.4–108.4°.

**9-Methyl-3,4-benzopyrene (VI).**—A mixture of 20 g. of sodium chloride, 75 g. of aluminum chloride and 10 g. of 3-benzoyl-8-methylperinaphthane was heated gradually in an oil-bath to 130° and then kept at 130–150° for four and one-half hours. The flask was stoppered loosely and the melt stirred frequently with a glass rod. The dark red melt was poured onto ice and acid, giving a very dark, gummy precipitate which could not be collected by filtration and which had to be washed by decantation. The dark tar was dried superficially by pressing it between filter papers and, since attempts to isolate a benzanthrone derivative from the mixture had proved fruitless, the total crude product was mixed with about 150 cc. of zinc dust in a small distillation flask with an attached receiver and this was sealed off and heated in a nitrite bath as long as any material distilled (one hour). A first fraction consisted of a dark red oil which did not crystallize, and a second was more viscous and partially solidified, giving 2 g. of crude solid product. The first fraction when treated with trinitrobenzene in benzene–ligroin afforded a small amount of crystalline product; this was recrystallized and decomposed by filtration of a benzene solution through an alumina tower, and the recovered hydrocarbon was combined with material obtained by passing the second fraction

from the distillation in benzene through alumina. Crystallization of the combined material from hexane gave a mixture which could be separated mechanically into yellow leaflets, m. p. 160–163°, and clumps of small needles, m. p. 145.5–147°. The higher melting material after three crystallizations from hexane melted at 172–174° and had all the characteristics of 3,4-benzopyrene (m. p. 178.5–179°). The lower melting material consisted of nearly pure 9-methyl-3,4-benzopyrene, and after two further crystallizations from hexane, this formed small, golden-yellow needles, melting initially at 146.8–148° and, after solidification, at 147.2–148° (40 mg.).

*Anal.*<sup>20</sup> Calcd. for C<sub>21</sub>H<sub>14</sub>: C, 94.70; H, 5.30. Found: C, 94.95; H, 5.44.

The trinitrobenzene derivative crystallized from benzene–ligroin as bright red needles, m. p. 218.5–219.5°.

When the zinc dust distillation was carried out at a lower temperature no high melting hydrocarbon was encountered and there was obtained along with 9-methyl-3,4-benzopyrene material melting at 124–134° and probably consisting of a mixture of hydrides.

**4' - Keto - 1',2',3',4' - tetrahydro - 3,4 - benzopyrene.**—Four and one-half grams of phosphorus pentachloride was added in fractions to a stirred solution of 5 g. of purified<sup>21</sup>  $\gamma$ -(1-pyrenyl)-butyric acid in 50 cc. of dry benzene and the solution was then warmed to the boiling point and refluxed for one hour. The clear solution was cooled to room temperature and treated with 2.5 cc. of stannic chloride in 5 cc. of dry benzene, added a few drops at a time, when the color changed from yellow to orange to red and purplish-red. After stirring for four hours at room temperature and for four hours under reflux, the complex was decomposed by adding ice and hydrochloric acid and stirring vigorously for about one hour. The benzene layer was then separated, washed with water and with soda solution, and the solvent removed by steam distillation. The residual solid when crystallized once from either glacial acetic acid or dioxane afforded 4.0–4.45 g. (85–95%) of yellow ketone, m. p. 163–165°, suitable for catalytic hydrogenation.

**Ozonization of Pyrene.** (a) **Phenanthrene-4-aldehyde-5-carboxylic Acid.**<sup>12</sup>—In a typical experiment a solution of 3 g. of pyrene in 75 cc. of purified ethyl acetate was treated at room temperature with a gas stream delivering ozone through a perforated bulb at the rate of 0.46 g. per hour. The solution was placed in a hydrogenation flask together with 1 g. of palladinized calcium carbonate<sup>14</sup> and shaken with hydrogen. After a lag of fifteen to thirty minutes the solution took up 75–100 cc. of gas in about one hour. When difficulty was experienced in starting the reaction, this was easily remedied by adding a trace of Adams catalyst. After hydrogenation the filtered solution was evaporated to a small volume and the acidic material extracted with 100 cc. of 5% alkali. On acidification of the filtered alkaline solution the aldehyde-acid separated as a clean solid and on crystallization from acetone formed colorless needles, m. p. 279–280°. The yield was 1.0 g. (27%) and considerable unreacted pyrene could be recovered from the neutral fraction.

The aldehyde-acid was the sole reaction product isolated in similar ozonizations conducted for brief periods

in pyridine (purified by refluxing with potassium hydroxide and with barium oxide) at room temperature or in ethyl chloride at –10°.

In a trial hydrogenation experiment 0.6 g. of the aldehyde-acid in 8 cc. of absolute ethanol with 50 mg. of copper chromite catalyst was shaken at 130° with hydrogen at an initial pressure of 1400 lb. for four hours. Concentration of the filtered solution gave crystals melting at 170–172°, and when this material was extracted with alkali and the residue crystallized from alcohol there was obtained silky needles, m. p. 177.5–178°. The analysis and neutral character of the substance indicate that it probably is the ethyl ester of 4-hydroxymethylphenanthrene-5-carboxylic acid.

*Anal.* Calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>: C, 77.12; H, 5.75. Found: C, 77.10; H, 5.56.

(b) **Biphenyl - 2,2',6,6' - tetraaldehyde.**—The ozonization of 3 g. of pyrene in 75 cc. of ethyl acetate was conducted at 0° for one and one-half hours with a gas stream delivering 0.82 g. of ozone per hour. After hydrogenative decomposition as above, the filtered solution was concentrated in vacuum to a volume of 15–20 cc., hot water was added, the organic solvent was boiled off, the aqueous solution was digested with Norit and filtered from an undissolved residue. The first crop of crystals which separated on cooling consisted largely of the tetraaldehyde, and subsequent crops appeared to be mixtures of this substance and the tetracarbinol. The first crystallate consisted of colorless, shiny flakes, m. p. 162.2–163.2° (0.5 g.). The analytical sample after several recrystallizations from benzene–hexane melted at 162–162.8°.

*Anal.*<sup>22</sup> Calcd. for C<sub>16</sub>H<sub>10</sub>O<sub>4</sub>: C, 72.18; H, 3.78. Found: C, 72.02; H, 3.87.

Reaction with phenylhydrazine gave a poorly crystalline product, m. p. 193–197°. Treatment with hydroxylamine hydrochloride and sodium acetate in water gave a derivative which crystallized from water as colorless plates, m. p. 237°, dec., and which appears from the analyses to be a monoacetate of the tetraoxime.

*Anal.*<sup>22</sup> Calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>N<sub>4</sub>: C, 58.71; H, 4.38; N, 15.21. Found: C, 58.86; H, 4.17; N, 15.22.

(c) **2,2',6,6' - Tetra - (hydroxymethyl) - biphenyl.**—This was most easily isolated by conducting the ozonization as in (b) but continuing the hydrogenation of the ozonide for a prolonged period (two hours). Extraction of the collected product with hot water gave 0.4 g. of material which crystallized from water in colorless plates, m. p. 171.2–172°.

*Anal.*<sup>22</sup> Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>: C, 70.04; H, 6.62. Found: C, 70.00; H, 6.96.

**Hydrogenation of Pyrene.**—The colorless commercial pyrene available gave no test for sulfur by the sodium nitroprusside method but resisted hydrogenation. Using a more sensitive basic lead acetate method suggested by Dr. E. B. Hershberg, a faint positive test for sulfur was obtained. The hydrocarbon (25 g.) was consequently stirred with sodium (2.5 g.) at 210–230° for three hours, extracted with benzene (three hours refluxing), and the filtered solution was clarified with Norit and the collected product dis-

(20) Microanalysis by Lyon Southworth.

(21) Fieser, Fieser and Hershberg, *TITIS JOURNAL*, **58**, 1463 (1936).

(22) Microanalysis by Herbert S. Wight.

tilled and crystallized from alcohol. The hydrocarbon (m. p. 147–148°),<sup>23</sup> recovered in 75% yield, gave no test for sulfur by the second method and could be hydrogenated rapidly.

In experiments conducted with 5 g. of purified pyrene and 0.25 g. of copper chromite catalyst in a glass liner at initial pressure of 1700–1900 lb. a hydrogen uptake calculated for the tetrahydride stage was reached in fifteen minutes at 190°, in one hour at 160°, and, using 30 cc. of absolute alcohol as solvent, in one and one-half hours at 108°. There was no significant difference in the reaction mixtures obtained. In the experiment conducted at 108° the collected product when crystallized from alcohol gave in the first crop 1.8 g. of long, spar-like needles of *s*-hexahydropyrene. The recrystallized material melted at 133.8–134.4° and showed no depression when mixed with a purified sample of the hydrocarbon (m. p. 133–134°) prepared

(23) Observations in our laboratory fail to confirm the high m. p. (156°, corr.) for purified pyrene reported by Winterstein, Schön and Vetter, *Z. physiol. Chem.*, **230**, 158 (1934). The most extensively purified sample used by Baxter and Hale, *THIS JOURNAL*, **59**, 506 (1937), in their atomic weight work was found by Dr. E. B. Hershberg to melt at 150.5–150.8°, corr. Dr. Hershberg subsequently prepared a better, sulfur-free sample by fusion of yellow commercial pyrene with maleic anhydride, distillation, treatment with alkali and then with sodium, and crystallization. The sample was colorless and melted at 150.9–151.1°, corr.

by reduction with sodium and amyl alcohol.<sup>16</sup> A second crop of flaky crystals (1.3 g.) melted at 98–102° and on treatment with picric acid in alcohol afforded first 0.45 g. of red pyrene picrate, m. p. 218–220°. A more soluble picrate crystallized from benzene–ligroin as orange needles, m. p. 146–147° (1.6 g.), and afforded a hydrocarbon (0.35 g.) crystallizing from alcohol in small plates, m. p. 103–105°. This corresponds to the substance isolated by Coulson<sup>15</sup> (m. p. 106°, picrate 148°) and regarded as *as*-tetrahydropyrene. A third crystallizate (1.5 g.) melting at 87–93.5° was not identified.

### Summary

9-Methyl-3,4-benzpyrene has been synthesized by application of the Scholl ring closure, with subsequent zinc dust distillation, to the benzoyl derivative of 8-methylperinaphthane. The intermediate hydrocarbon was obtained in good yield by synthesis from  $\alpha$ -chloromethylnaphthalene and ethyl methylmalonate.

Observations are reported concerning the ozonization and hydrogenation of pyrene.

CONVERSE MEMORIAL LABORATORY

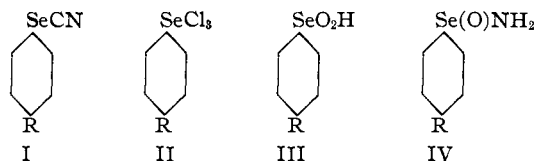
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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

## Organoselenium Compounds. II. Derivatives of Phenylseleninic Acid and Phenylseleninamide

By C. KENNETH BANKS<sup>1</sup> AND CLIFF S. HAMILTON

In a previous paper<sup>2</sup> the preparation of several series of diphenylselenium dihydroxides and diphenylselenides was reported. This study has been continued into other valencies of selenium, including the diselenides, seleninic acids and selenonic acids. The three series of derivatives considered were the *p*-nitro, acetamino and amino compounds.



Selenium was introduced into the benzene nucleus by Bauer's modification<sup>3</sup> of the Sandmeyer reaction, giving the selenocyanate (I). *p*-Nitrophenylselenocyanate was prepared by the procedure of Bauer<sup>3</sup> and *p*-acetaminophenylselenocy-

anate by that of Challenger and Peters.<sup>4</sup> The product reported by Bauer was found to contain an impurity which could be removed by solution in cold concentrated nitric acid and reprecipitation with water. *bis*-(4-Nitrophenyl) diselenide was prepared by the method of Behagel and Siebert<sup>5</sup> and the corresponding acetamino compound was formed by a reaction similar to the method introduced by Behagel and Rollmann.<sup>6</sup> *bis*-(4-Aminophenyl) diselenide had been made by Keimatsu and Satoda<sup>7</sup> from *p*-nitrophenylselenocyanate but it was more conveniently prepared from *bis*-(4-nitrophenyl) diselenide by catalytic reduction.

The seleninic acids (III) were obtained by the oxidation of the selenocyanate to the selenium trichloride (II) and subsequent hydrolysis.<sup>3</sup> Formation of amides of seleninic acids (IV) has never been reported, so particular conditions, starting products and reagents were necessary in each case.

(1) Parke, Davis and Company Fellow.

(2) C. K. Banks and C. S. Hamilton, *THIS JOURNAL*, **61**, 2306 (1939).

(3) Bauer, *Ber.*, **46**, 93 (1913).

(4) Challenger and Peters, *J. Chem. Soc.*, 1375 (1928).

(5) Behagel and Siebert, *Ber.*, **66**, 708 (1933).

(6) Behagel and Rollmann, *J. prakt. Chem.*, **123**, 326 (1930).

(7) Keimatsu and Satoda, *J. Pharm. Soc. Japan*, **56**, 600 (1936).