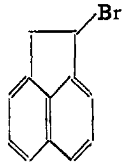
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# The Synthesis of 4,5-Methylenephenanthrene

BY W. E. BACHMANN AND JOHN CLARK SHEEHAN[1]

The hydrocarbon 4,5-methylenephenanthrene (VI) was isolated in 1934 by Kruber[2] from the refined neutral fraction of anthracene oil. The oxidation products of the compound have been studied by Kruber, and the succinoylation derivatives have been investigated by Fieser and Cason.[3] However, 4,5-methylenephenanthrene has not been available by synthesis. Von Braun and Roth[4] succeeded in synthesizing an octahydro-4,5-methylenephenanthrene, but they were unable to dehydrogenate it to 4,5-methylenephenanthrene. A method has now been devised whereby this hydrocarbon can be prepared fairly easily.

The readily available acenaphthene was oxidized to 7-acenaphthenol, which, by interaction with phosphorus tribromide, was converted to 7-bromoacenaphthene (I). The bromide was condensed with sodio-malonic ester to give 7-acenaphthylmalonic acid in good yield. 7-Acenaphthylacetic acid (II), obtained by decarboxylation of the substituted malonic acid, was converted to β-(7-acenaphthyl)-propionic acid (III) by lengthening the side chain by means of the Arndt–Eistert reaction. Cyclization through the acid chloride with stannic chloride afforded an excellent yield of the cyclic ketone (IV), which was then reduced to 1-hydroxy-4,5-methylene-1,2,3,4-tetrahydrophenanthrene by the aluminum isopropoxide method. The alcohol was smoothly dehydrated and dehydrogenated to 4,5-methylenephenanthrene when heated with palladium on charcoal. The hydrocarbon was obtained also by Clemmensen reduction of the ketone (IV) to the tetrahydro compound, which was then dehydrogenated to VI in good over-all yield.



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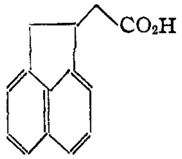

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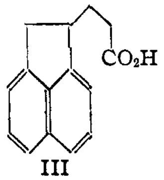

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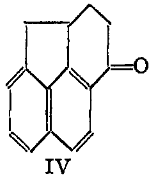

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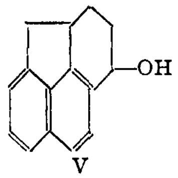

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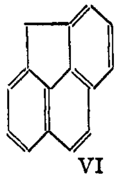

VI

## Experimental

**7-Bromoacenaphthene (I).**—To a cooled solution of 6 g. of 7-acenaphthenol[5] in 50 cc. of anhydrous ether was added 1.23 cc. of phosphorus tribromide. After standing one-half hour, the mixture was hydrolyzed. The ethereal layer was washed with water, sodium bicarbonate solution, and again with water. The solution was dried over magnesium sulfate, filtered, and the ether removed under reduced pressure (40°). The residual oil solidified immediately. Digestion of the crude bromide with 30–60° petroleum ether left 6.75 g. of yellowish leaflets; m. p. 70.5–71.5°. From the extract 0.53 g. of only slightly less pure product was isolated, making a total yield of 89%. The bromide is unstable, and should be prepared only as needed.

*Anal.* Calcd. for $C_{12}H_9Br$: Br, 34.4. Found: Br, 33.8.

**7-Acenaphthylmalonic Acid.**—A cooled solution of the crude 7-bromoacenaphthene from 20 g. of 7-acenaphthenol in 75 cc. of dry benzene was added to a cooled solution of sodio-malonic ester prepared from 35.6 cc. of malonic ester and 7.06 g. of sodium in 250 cc. of absolute alcohol. The mixture was kept in a refrigerator for three days, and then refluxed for two hours. The solvents were evaporated, and the ester was hydrolyzed by warming for one-half hour on a steam-bath with 125 cc. of 40% potassium hydroxide solution. After dilution with an equal volume of water, the solution was refluxed for an additional hour and one-half, cooled, and filtered through glass wool. Acidification precipitated 24.55 g. (82%, based on the 7-acenaphthenol) of fine colorless needles of the substituted malonic acid; m. p. 174–175°.

*Anal.* Calcd. for $C_{15}H_{12}O_4$: C, 70.3; H, 4.7. Found: C, 70.2; H, 4.6.

**7-Acenaphthylacetic Acid (II).**—Thirty grams of the 7-acenaphthylmalonic acid was heated at 190° for one-half hour. The melt was poured into acetone while still warm, the solution treated with Norit, filtered, the solvent evaporated off, and the acid crystallized from benzene–petroleum ether (1:4). The first crop of colorless platelets weighed 21.56 g.; m. p. 115–116°. An additional 2.26 g. of only slightly less pure product brought the total yield of crystalline material to 96%.

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(1) From the Ph.D. dissertation of John Clark Sheehan.

(2) Kruber, *Ber.*, **67**, 1000 (1934).

(3) Fieser and Cason, THIS JOURNAL, **62**, 1293 (1940).

(4) Von Braun and Roth, *Ber.*, **61**, 956 (1928).

(5) Fieser and Cason, THIS JOURNAL, **62**, 432 (1940).

A sample after sublimation at 160° and 0.5 mm. and recrystallization from benzene–petroleum ether melted at 116–117°.

*Anal.* Calcd. for $C_{14}H_{12}O_2$: C, 79.3; H, 5.7. Found: C, 78.8; H, 5.7.

**β-(7-Acenaphthyl)-propionic Acid (III).**—To 10 g. of 7-acenaphthylacetic acid in 50 cc. of anhydrous ether and 2 drops of pyridine was added 4.4 cc. of thionyl chloride, and the mixture was allowed to stand for two hours with occasional swirling. The solvent and excess of reagent were removed under reduced pressure. Ten cubic centimeters of dry benzene was added and then removed by a second evaporation. A solution of the acid chloride in 50 cc. of dry ether was decanted dropwise (through a small cotton plug in the side arm of a flask) into 300 cc. of a chilled solution of diazomethane prepared from 30 g. of nitrosomethylurea.

After one hour the ether was removed under reduced pressure, and the crystalline diazo ketone was added to a mixture of 50 cc. of absolute methanol and 0.5 g. of silver oxide (Mallinckrodt U. S. P.) which had been refluxed previously until a silver mirror had formed (three minutes). After the mixture had been refluxed for one-half hour, another 0.5-g. portion of silver oxide was added and the heating continued for a total of one and one-half hours. Treatment with Norit and Filter-Cel, followed by filtration, gave a light yellow solution. This was refluxed one hour with 10 cc. of a 40% sodium hydroxide solution. The methanol was evaporated off, the sodium salt taken up in water, the solution boiled with Norit, filtered and acidified. The acid was crystallized from dilute acetic acid, weight 7.45 g.; m. p. 102.5–104.5°. Cyclization (as described below) of crude acid in the filtrate gave 0.84 g. (representing 0.91 g. of acid) of good cyclic ketone, making a total yield of 78%. A sample after distillation at 160° and 0.5 mm. crystallized from acetone–petroleum ether in colorless platelets which melted at 108.5–109.5°.

*Anal.* Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.2. Found: C, 79.7; H, 6.1.

**1 - Keto - 4,5 - methylene - 1,2,3,4 - tetrahydrophenanthrene (IV).**—Seventeen grams of phosphorus pentachloride was added to a solution of 13 g. of β-(7-acenaphthyl)-propionic acid in 100 cc. of benzene. After thirty minutes the solution was cooled in ice and 13 cc. of stannic chloride was added. After fifteen minutes the brown complex was hydrolyzed with ice and hydrochloric acid. The organic layer was washed with hydrochloric acid, water, twice with 10% potassium hydroxide, and again with water. After removal of the benzene the ketone was crystallized from 60–75° petroleum ether containing a little acetone. The first crop of yellowish rhombs weighed 10.04 g.; m. p. 122–123°. A somewhat lower melting second crop of 1.01 g. brought the yield of recrystallized product to 92%. A sample after distillation at 150° (0.01 mm.) and recrystallization from acetone–petroleum ether was colorless and melted at 124.5–125.5°. The ketone gives a light orange color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.6; H, 5.8. Found: C, 86.3; H, 5.8.

**1 - Hydroxy - 4,5 - methylene - 1,2,3,4 - tetrahydrophenanthrene (V).**—A mixture of 2 g. of the aforementioned ketone and 50 cc. of a *M* solution of aluminum isopropoxide in anhydrous isopropyl alcohol was refluxed for one-half hour. Thirty-five cubic centimeters of liquid was distilled off slowly over a two-hour period; at the end of this time no test for acetone could be obtained in the distillate with 2,4-dinitrophenylhydrazine reagent.

The viscous residue was poured into 250 cc. of ice water containing 10 cc. of sulfuric acid. The solid was filtered off, washed thoroughly with dilute ammonia and water, and dried. The crude alcohol was dissolved in benzene, the solution treated with Norit, and filtered. Crystallization from petroleum ether–acetone gave 1.42 g. of very fine, colorless needles; m. p. 112–113°. An additional 0.33 g. of only slightly less pure product isolated from the filtrate brought the yield to 87%. A sample after two recrystallizations from acetone–petroleum ether melted at 113–114°. The alcohol gave a dark reddish-brown color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.8; H, 6.7.

**4,5-Methylenephenanthrene (VI).** **(a) From 1-Hydroxy-4,5 - methylene - 1,2,3,4 - tetrahydrophenanthrene.**—A mixture of 2 g. of 1-hydroxy-4,5-methylene-1,2,3,4-tetrahydrophenanthrene and 0.2 g. of palladium–charcoal catalyst[6] was heated in a nitrogen atmosphere at 280–300° for one-half hour. The product was extracted with benzene, filtered, and the solvent removed by evaporation. Distillation at 160° (0.5 mm.) gave 1.55 g. (86%) of colorless plates; m. p. 114–115°. One recrystallization from alcohol raised the melting point to 114.3–115.3°. The picrate melted at 165.8–166.5°. Kruber[2] reported melting points of 116° and 166° for the hydrocarbon and picrate, respectively. The melting point of the hydrocarbon was undepressed when mixed with a sample of 4,5-methylenephenanthrene (m. p. 114.0–115.0°) isolated from coal tar by Kruber and kindly furnished by Dr. L. F. Fieser. Likewise, there was no depression in the melting point of the picrate when mixed with the picrate of Kruber's hydrocarbon.

**(b) From 4,5-Methylene-1,2,3,4-tetrahydrophenanthrene.**—Six grams of 1-keto-4,5-methylene-1,2,3,4-tetrahydrophenanthrene was added to a mixture of 15 g. of amalgamated zinc, 10 cc. of water, 30 cc. of hydrochloric acid, 4 cc. of glacial acetic acid and 15 cc. of toluene. After thirty-six hours of refluxing, during which time two 5-cc. portions of hydrochloric acid were added, the organic layer was separated and the aqueous layer diluted and extracted with benzene. The tetrahydro derivative obtained by removal of the benzene partially solidified. Without purification it was heated with 0.4 g. of palladium–charcoal catalyst in a nitrogen atmosphere at 280–300° for one hour. The crude product was extracted with acetone and filtered. After removal of the solvent, the residue was distilled at 175° and 0.5 mm. and recrystallized from alcohol, yielding 2.52 g. (52%, based on the cyclic ketone) of 4,5-methylenephenanthrene as colorless, nacreous plates; m. p. 114–115°.

**4,5 - Methylene - 1,2,3,4 - tetrahydrophenanthrene.**—To a mixture of 4 g. of amalgamated 20-mesh zinc, 15 cc. of water, 8 cc. of hydrochloric acid, 2 cc. of glacial acetic acid and 4 cc. of toluene was added 1 g. of 1-keto-4,5-methylene-

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[6] Zelinsky and Turowa-Pollak, *Ber.*, 58, 1295 (1925).

1,2,3,4-tetrahydrophenanthrene. After twenty-four hours of refluxing, the mixture was diluted, the organic layer separated, and the aqueous layer extracted with benzene. The residue remaining after removal of solvent from the combined extracts was distilled at 160° and 0.5 mm. The colorless distillate crystallized on cooling, weight 0.59 g. (63%); m. p. 54.5–55.5°. A sample recrystallized from alcohol gave fine, colorless prisms; m. p. 55.5–56.5°.

*Anal.* Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.2.

The **picrate** crystallized from alcohol as orange-red needles; m. p. 159–160°.

*Anal.* Calcd. for $C_{21}H_{17}O_7N_5$: N, 9.9. Found: N, 9.8.

## Summary

A method has been devised for the preparation of 4,5-methylenephenanthrene from acenaphthene.

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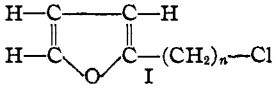
[Contribution from the William H. Chandler Chemistry Laboratory, Lehigh University]

# 2-α-Furylethanol and 2-α-Furylethyl Chloride

By E. D. Amstutz and Julius Plucker, III

In recent years furfuryl alcohol has become one of the most readily available of furan derivatives. Its higher homolog, 3-α-furylpropanol, is also easily obtained[1] by catalytic reduction of furylacrolein. These compounds may be converted into the corresponding chlorides in satisfactory yield by the method of Kirner.[2]

Furfuryl chloride (I, $n = 1$) when treated with magnesium in ether has been reported[3] to yield, as one of the products, *sym*-difurylethane. The formation of this compound indicates rather strongly that a Grignard reagent was actually formed. Its further reaction with furfuryl chloride is understandable in view of the reactive halogen in that compound. Nevertheless, it would appear that conditions have not been found under which the Grignard reagent is of use synthetically in reactions other than the one mentioned. Unsuccessful attempts to prepare the Grignard reagent from 3-α-furylpropyl chloride (I, $n = 3$) also have been reported,[4] although it is probable that failure in this case was not due to great reactivity of the halogen.



I

It has recently been found that ethyl 2-furanacetate on reduction with sodium and alcohol gives 2-α-furylethanol.[5] This alcohol, which is produced in yields of about 32% of the theoretical, is a water-white liquid of stability comparable to that of the propanol. The synthesis of 2-α-furylethyl chloride (I, $n = 2$) was accomplished in the usual manner by treatment of the alcohol with thionyl chloride in the presence of ether and pyridine. Like the propyl chloride, the ethyl chloride is somewhat unstable, turning dark and depositing a black oil after standing several days at room temperature. In contrast to its adjacent compounds in the homologous series it reacts with magnesium to give a stable and usable Grignard reagent.

## Experimental

**2-α-Furylethanol.**—A solution of 32.8 g. (0.213 mole) of ethyl 2-furanacetate in 360 cc. (7.83 moles) of absolute ethyl alcohol was dropped during the course of twenty minutes onto 31.2 g. (1.36 g. atoms) of sodium metal in a one-liter flask in an oil-bath heated to 145°. Heating was continued for twenty minutes after the addition and a further 60 cc. of absolute alcohol was added. The addition of 60 cc. of alcohol was repeated fifteen minutes later. Heating was then continued until all the sodium had dissolved. The dark red solution was cooled slightly and rapidly steam distilled until about 350 g. of distillate had been collected. The residue remaining in the flask was then saturated with salt and extracted with seven 50-cc. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate and distilled: 2-α-Furylethanol (7.8 g., 32% of the theoretical), b. p. 86–88° at 21 mm., 96–97° at 42 mm., $n^{25}_{D}$ 1.4788, $d^{25}_{4}$ 1.0705, $MR_D$ (calcd.) 29.94, $MR_D$ (obsd.) 29.66.

*Anal.* Calcd. for $C_6H_8O_2$: C, 64.23; H, 7.19. Found: C, 64.26; H, 6.92.

**α-Naphthylurethan of 2-α-furylethanol**, m. p. 85.2–86° (from ligroin).

*Anal.* Calcd. for $C_{17}H_{15}O_3N$: C, 72.57; H, 5.38. Found: C, 72.85; H, 5.72.

**2-α-Furylethyl Chloride.**—Into a solution of 7.8 g. (0.067 mole) of furylethanol and 6.6 g. (0.084 mole) of pyridine and 25 cc. of dry ether in a 200-cc. 3-necked flask provided with a mechanical stirrer, reflux condenser and dropping funnel was added dropwise over a period of forty-five

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(1) Bray and Adams, This Journal, **49**, 2101 (1927).

(2) Kirner, *ibid.*, **51**, 3131 (1929).

(3) Gilman and Hewlett, *Rec. trav. chim.*, [4] **51**, 93 (1932).

(4) Ref. 3 and Hewlett, *Iowa State Col., J. Sci.*, **6**, 439 (1935).

(5) Ryan. Plucker and Amstutz, This Journal, **62**, 2037 (1940).