hydrolysis of the anhydride is very little soluble in hot water.

1,2-Benzanthracene-9,10-endo-α,β-succinic anhydride was isolated by heating a mixture of 0.4 g. of 1,2-benzanthracene and 5 g. of maleic anhydride in 8 cc. of boiling benzene for three hours, evaporating the solution, subliming the maleic anhydride from the mixture at 80° at 0.4 mm. and washing the residue with benzene; yield, 0.26 g. Our product agreed in properties with that reported by Clar.[11]

Dimethyl Ester of 1,2,5,6-Dibenzanthracene-9,10-*endo*-α,β-succinic Acid.—Cook[6] prepared the acid from the adduct obtained by fusing equimolecular proportions of 1,2,5,6-dibenzanthracene and maleic anhydride. He found that most of the hydrocarbon was recovered unchanged when it was heated with half its weight of maleic anhydride in boiling xylene for five hours. As Table II shows, the compound can be obtained in 90% yield in one hour if thirty mole equivalents of maleic anhydride are employed. The dimethyl ester of the dicarboxylic acid was prepared by the action of diazomethane on a suspension of the unrecrystallized acid in acetone. From ethyl acetate the ester crystallized in colorless needles; m. p. 230–231°.

Anal. Calcd. for $C_{26}H_{16}O_3$: C, 79.6; H, 5.3. Found: C, 79.2; H, 5.3.

3-Methylcholanthrene-6,12b-*endo*-α,β-succinic Anhydride.—This compound is best prepared in benzene since some decomposition occurs in boiling xylene. A bright-red color, presumably of a molecular complex, is formed on mixing 3-methylcholanthrene and maleic anhydride in a solvent; as the addition reaction proceeds, the red color disappears. When a mixture of 1 g. of 3-methylcholanthrene and 0.5 g. of maleic anhydride in 10 cc. of benzene was refluxed for two days and then cooled, 0.8 g. of the adduct crystallized from the solution in large, transparent prisms. From ethyl acetate the anhydride crystallized in colorless needles; m. p. 209–210° with decomposition.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.9; H, 4.9. Found: C, 81.6; H, 4.9.

The dicarboxylic acid which was obtained from the anhydride by hydrolysis with potassium hydroxide followed by treatment of the salt with hydrochloric acid dissolved readily in cold ethyl acetate; no crystallization took place when the solution was allowed to evaporate. When, however, the solution was heated at the boiling point for a few minutes and then cooled, immediate crystallization of colorless needles of the anhydride took place.

When a solution of 135 mg. of 3-methylcholanthrene-6,12b-*endo*-α,β-succinic anhydride in 2 cc. of xylene was refluxed for thirty minutes, a 78% yield of 3-methylcholanthrene was formed. By employing a larger volume of solvent it should be possible to effect nearly complete dissociation of the adduct and the procedure offers a method of purifying methylcholanthrene. The regenerated methylcholanthrene possessed a pale yellow color. By heating a solution of 135 mg. of the adduct in 2 cc. of benzene for twenty-four hours, a 6% yield of 3-methylcholanthrene was obtained.

The **dimethyl ester** of 3-methylcholanthrene-6,12b-*endo*-α,β-succinic acid was prepared by the action of diazomethane on an acetone solution of the dicarboxylic acid freshly precipitated from the aqueous solution of its potassium salt. From ethyl acetate the ester crystallized in colorless needles; m. p. 165.5–166.5°.

Anal. Calcd. for $C_{27}H_{24}O_4$: C, 78.6; H, 5.9. Found: C, 78.6; H, 5.8.

Summary

The effect of concentration, time and temperature on the yields of adduct formed in the Diels–Alder reaction between maleic anhydride and eight polycyclic hydrocarbons containing the anthracene nucleus has been determined.

It has been established that in boiling xylene an equilibrium is established in virtue of the reversible reaction. Procedures have been worked out for securing excellent yields of the adducts.

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 27, 1937

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(11) Clar, *Ber.*, **65**, 519 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Synthesis of 3,4-Benzphenanthrene

BY MELVIN S. NEWMAN AND LLOYD M. JOSHEL[1]

Of the four possible tetracyclic aromatic hydrocarbons of the formula $C_{18}H_{12}$, namely, 1,2-benzanthracene I, 3,4-benzphenanthrene II, chrysene III, naphthacene IV, and triphenylene V, only the first has been much studied from the point of view of the effect of chemical constitution on carcinogenic activity. Itself inactive, the latent carcinogenic properties of the 1,2-benzanthracene nucleus are developed to a remarkable degree in certain of its derivatives. For example, methylcholanthrene, which may be considered as a 5,6,10-trisubstituted 1,2-benzanthracene, is the most potent carcinogenic hydrocarbon known, and certain other derivatives, all containing groups on the *meso*-positions, approach methylcholanthrene in their ability to induce sarcoma (cancer of connective tissue) in mice.[2]

Since certain derivatives of I are potent cancer-

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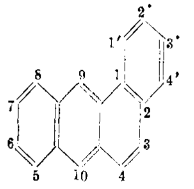
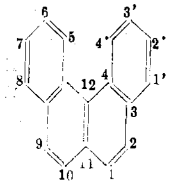
[1] Ohio State University Fellow.

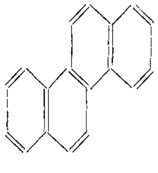
[2] For reviews on the subject of carcinogenic activity see: (a) Barry, Cook, *et al.*, *Proc. Roy. Soc.* (London), **B117**, 318 (1935); (b) Bachmann, Cook, *et al.*, *ibid.*, **B123**, 343 (1937); (c) Fieser, *et al.*, *Am. J. Cancer*, **29**, 260 (1937).



I



II



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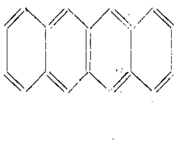

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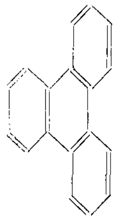
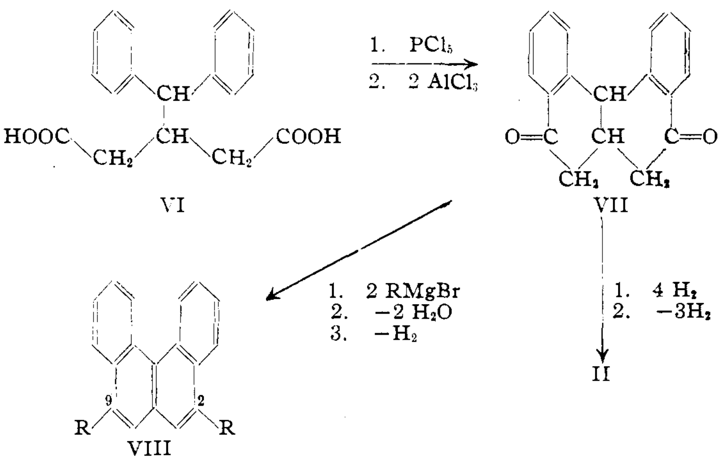


V

producing agents, it would seem appropriate to investigate similar derivatives of all of the other members of this class of tetracyclic hydrocarbons. It seemed particularly interesting to study derivatives of 3,4-benzphenanthrene (II), which itself has been reported to be somewhat active.[2a] The importance of preparing derivatives of II has been emphasized by the recent finding that 2-methyl-3,4-benzphenanthrene[3] is a potent carcinogenic agent.[2b]

The synthesis of 3,4-benzphenanthrene, II, and its derivatives has been exceedingly difficult to date and no truly satisfactory general method is yet available.[4] The work herein reported was undertaken in an effort to find a method suitable for the preparation of variously substituted derivatives of 3,4-benzphenanthrene. The scheme of synthesis is illustrated by the following diagrams.



Owing to unexpected difficulties in the preparation of the starting material, β-benzohydrylglutaric acid, VI, we have carried through the remaining steps in the synthesis on a small scale in order to see whether it was worth while to continue work on the proposed synthesis. The results proved encouraging, and we are now engaged in studying methods by which V and similar acids may be prepared in larger quantities. Using the above method, we have prepared II, 2,9-dimethyl-3,4-benzphenanthrene (VIII, R = CH_3) and 2,9-diethyl-3,4-benzphenanthrene (VIII, R = C_2H_5).

The diketone, VII, was prepared in 52% yield by a double ring-closure (Friedel-Crafts) of the acid chloride of VI. The 2,9-dimethyl and 2,9-diethyl homologs were prepared in 47 and 42% over-all yields by treating the diketone VII with an excess of the appropriate Grignard reagents, dehydration of the resulting carbinols, and subsequent dehydrogenation. No attempt was made to isolate the intermediate compounds owing to the small scale of operations. By Wolff-Kishner reduction of the disemicarbazone of VII, followed by catalytic dehydrogenation, we obtained a small amount of 3,4-benzphenanthrene, II.

The new compounds are being tested for carcinogenic activity by Dr. M. J. Shear.[5]

Experimental[6]

β-Benzohydrylglutaric Acid, VI.—In a typical experiment, 1 cc. of diethylamine and two drops of acetic acid were added to an ice-cold solution of 5 g. of diphenylacetaldehyde[7] in 21 g. of ethyl cyanoacetate. The mixture soon became cloudy owing to the formation of water. After standing at room temperature for twelve hours, it was heated on the steam-bath for ten hours. The reaction mixture was worked up in two ways: one involved saponification with alcoholic sodium hydroxide until ammonia was no longer evolved (thirty hours); the other involved hydrolysis with a mixture of sulfuric acid, acetic acid, and water for periods ranging from forty-two to

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[3] Hewett, *J. Chem. Soc.*, 596 (1936).

[4] The following publications contain accounts of successful or unsuccessful attempts at the synthesis of II or its derivatives: (a) Weitzenböck and Lieb, *Monatsh.*, **33**, 564 (1912); (b) Mayer and Oppenheimer, *Ber.*, **51**, 510 (1918); (c) Cook, *J. Chem. Soc.*, 2524 (1931); (d) Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935); (e) Fieser, Fieser and Hershberg, *ibid.*, **58**, 1463 (1936); (f) Adelson and Bogert, *ibid.*, **59**, 177 (1937); (g) Fieser and Dunn, *ibid.*, **59**, 1024 (1937).

[5] A communication from Dr. Shear stated that 6,7-dimethyl-3,4-benzphenanthrene[4e] has produced no tumors after sixteen months.

[6] All melting points corrected. Analyses marked * semi-micro by H. S. Clark; † micro by Arlington Laboratories, Arlington, Va. The authors are indebted to Dr. W. M. MacNevin for the micro Dumas analyses marked ‡.

[7] Danilova and Venus-Danilova, *Ber.*, **59**, 1037 (1926); Thomas and Bettzieche, *Z. physiol. Chem.*, **140**, 244 (1924).

seventy-two hours. The crude acid was decarboxylated by heating and the desired acid, VI, either crystallized directly or after conversion to the methyl ester, distillation, and hydrolysis. The yield of acid melting over a one degree range varied from 12 to 21%. On recrystallization from acetone–benzene, the acid, VI, formed white needles, m. p. 177.6–178.2°.

*Anal.** Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08; neut. equiv., 149. Found: C, 72.66; H, 6.01; neut. equiv., 147.

The anhydride was made by refluxing the acid with acetyl chloride and crystallization of the product from acetic anhydride. It melted at 177.0–177.4° and gave a depression of 16° when mixed with the acid, V.

*Anal.** Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.96; H, 5.95.

2,9 - Diketo-1,2,9,10,11,12-hexahydro-3,4-benzphenanthrene, VII.—In a small pyrolysis flask with a sealed-on receiver were mixed 2.0 g. (0.0067 mole) of VI and 3.0 g. (0.014 mole) of phosphorus pentachloride. A clear, light yellow solution resulted when the mixture was heated thirty minutes on the steam-bath. After removing the phosphorus oxychloride and excess pentachloride by vacuum distillation, the residue was dissolved in 20 cc. of tetrachloroethane, cooled in an ice-bath, and 2.0 g. (0.015 mole) of powdered anhydrous aluminum chloride added in portions with shaking. The solution, which quickly turned dark red and soon evolved hydrogen chloride, was allowed to stand at room temperature for twelve hours and then was kept at 45–60° for four hours. The reaction mixture was decomposed with ice and hydrochloric acid, and the tetrachloroethane removed in a current of steam. On cooling, the solid was collected by filtration, powdered, and washed with ether. By dissolving this crude product in acetic acid or dioxane, the diketone, VII, crystallized in beautiful prisms. The yield of recrystallized product, sintering at 231.6° and melting at 234.0–234.4°, was 0.91 g. or 51.7%.

*Anal.** Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.54; H, 5.31.

The disemicarbazone was made by refluxing an aqueous dioxane solution of the diketone (0.50 g.), semicarbazide hydrochloride (0.85 g.) and sodium acetate (1.15 g.) for two hours. The solution was diluted with water and the small amount of amorphous material which precipitated first was filtered. On standing, 501 mg. of pale yellow spheres deposited. A second crop of 31 mg. was obtained, making the total yield 74%. As this compound was insoluble in all the common solvents, a sample was purified for analysis by digestion with dioxane. When put in a melting point bath at 260°, the compound decomposes at 266–268°, with an increase in volume, but no appreciable darkening.

Anal.‡ Calcd. for $C_{20}H_{20}O_2N_6$: N, 22.3. Found: N, 22.0.

3,4-Benzphenanthrene, II.—A solution of sodium ethoxide from 0.5 g. of sodium in 7 cc. of absolute alcohol was poured on 563 mg. of the disemicarbazone in a glass tube. The tube was placed in a steel tube and heated at 175–185° for ten hours. As all of the disemicarbazone had not reacted, the supernatant liquid was decanted and the residue treated as above with a fresh solution of sodium ethoxide. By vacuum distillation of the hydrocarbon fraction there was obtained 265 mg. of a pale yellow oil. After heating at 315–320° for seven hours with the platinum black obtained by reducing 0.1 g. of Adams catalyst the mixture was vacuum distilled. On treatment of the distillate with 0.5 g. of picric acid in benzene there was obtained 235 mg. of red needles, m. p. 122–124° (lit.[3] 126–127°, uncorr.). A portion recrystallized from benzene–ligroin melted at 125.8–126.2°. The hydrocarbon II was obtained as colorless needles, m. p. 65.6–66.2° (lit.[3] 68° uncorr.), by crystallization from alcohol after removing the picric acid by passing through an absorption tower containing activated alumina.

2,9-Dimethyl-3,4-benzphenanthrene, VII, R = CH_3.—A solution of 0.70 g. (0.0027 mole) of VII in 30 cc. of dry xylene was treated with a filtered solution of methylmagnesium bromide (0.013 mole) with the immediate formation of a white precipitate. The mixture was refluxed for five hours, cooled, decomposed with ice and hydrochloric acid, and the aqueous layer was extracted once with ether. The combined ether and xylene solutions were washed and the solvents distilled. The residual light yellow oil was transferred to a 10-cc. distilling flask with a sealed-on receiver, a crystal of iodine added, and the flask heated in a fused salt-bath for fifteen minutes, the temperature of the bath being raised gradually from 180 to 250°. A small amount of water distilled from the mixture during this time. After cooling, 85 mg. (0.0027 mole) of sulfur was added, and the flask returned to the bath. Evolution of hydrogen sulfide started at 220° and the mixture was heated at 230–240° for twenty-five minutes. The residue was vacuum distilled at 3 mm. and the distillate crystallized immediately. The compound was deposited in colorless needles from benzene–methanol, a total yield of 324 mg. of recrystallized product, m. p. 128.6–130.4°, being obtained (47.4%). After passing a benzene solution of the hydrocarbon through a tower of activated alumina, the product melted at 130.6–131.0°.

Anal.† Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.52; H, 6.49.

The picrate formed dark red needles from benzene–petroleum ether, m. p. 164.6–165.0°.

Anal.† Calcd. for $C_{26}H_{19}O_7N_3$: C, 64.34; H, 3.95; N, 8.68. Found: C, 64.71; H, 4.02; N, 8.86.

2,9-Diethyl-3,4-benzphenanthrene, VIII, R = C_2H_5.—The diethyl compound was prepared in the same way as the dimethyl compound from VII (0.51 g.) and ethylmagnesium bromide (3 g. ethyl bromide), but was isolated through the *s*-trinitrobenzene compound. A portion of this compound recrystallized twice from benzene–ligroin formed orange needles melting at 182.4–183.2°.

Anal.‡ Calcd. for $C_{28}H_{23}O_6N_3$: N, 8.45. Found: N, 8.21.

The hydrocarbon was isolated by passing a benzene solution of the *s*-trinitrobenzene compound through a tower of activated alumina. On crystallization from benzene–methanol, large colorless prisms of m. p. 104.4–106.0° were obtained. The total yield of 2,9-diethyl-3,4-benzphenanthrene, isolated as such and as the *s*-trinitrobenzene complex, amounted to 42%. For analysis a sample of the hydrocarbon was recrystallized from benzene-methanol to a melting point of 106.4–107.0°.

*Anal.** Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.89, 92.96; H, 7.00, 6.92.

Summary

A new synthesis for hydrocarbons containing the 3,4-benzphenanthrene nucleus is described. The method is based on a double ring closure of β-benzohydrylglutaric acid to yield 2,9-diketo-1,2,9,10,11,12-hexahydro-3,4-benzphenanthrene. By reduction and dehydrogenation this diketone is converted into 3,4-benzphenanthrene, whereas by reaction with methyl- or ethylmagesium bromide followed by dehydration and dehydrogenation, the diketone is converted into 2,9-dimethyl- or 2,9-diethyl-3,4-benzphenanthrene, respectively.

COLUMBUS, OHIO RECEIVED DECEMBER 23, 1937

NOTES

An Obscure Reaction of Phosphorus Trichloride

BY ROBERT D. COGHILL

Two explosions occurring in the elementary organic laboratory this past Fall have prompted me to write this note as a warning to other teachers. The accidents occurred during the preparation of acetyl chloride from phosphorus trichloride and acetic acid. In each case the student was ignoring the printed directions and attempting to distil the acetyl chloride from the phosphorous acid residue with a free flame rather than with a hot water-bath. The phosphorous acid was thus locally overheated and exploded with sparks and a yellow flame, copious white fumes (probably phosphorus pentoxide), and the odor of phosphorus or phosphine.

In attempting to find an explanation for the phenomenon it was found that phosphorus trichloride, when evaporated in an open breaker on a steam-bath, caught fire spontaneously and burned with a yellow flame, leaving a large residue of phosphorus in the beaker. When the evaporation was carried out on an electric hot-plate the material did not burn and only a small residue of phosphorus was obtained. When the phosphorus trichloride was distilled from a distilling flask in a system protected from atmospheric moisture with a calcium chloride tube, only a faint trace of phosphorus remained.

It was thus evident that the flame and the phosphorus residue result from the reaction of phosphorus trichloride and water. Mellor[1] states that when phosphorous acid is heated, phosphine is produced. The latter is then alleged to react with phosphorus trichloride to form free phosphorus and hydrogen chloride. These reactions would serve to explain both the observed reaction of phosphorus trichloride and steam, and the laboratory explosions. In the latter cases, overheating of the phosphorous acid produced phosphine in sufficient quantity to blow out the stoppers, the gas subsequently igniting spontaneously.

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RECEIVED DECEMBER 23, 1937

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[1] J. W. Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., 1928, pp. 806, 1002–1003.

2,2,3,4-Tetramethylhexane and 3,3,5-Trimethylheptane[1]

BY NATHAN L. DRAKE AND L. H. WELSH

2,2,3,4-Tetramethylhexane (I) and 3,3,5-trimethylheptane (II) have been prepared by the hydrogenation of corresponding olefins. The olefins were obtained by the action of sulfuric acid on methylisopropylcarbinol,[2] and were hydrogenated during passage in a stream of hydrogen over a copper chromite catalyst. Attempts to hydrogenate the olefins in the liquid phase using Adams platinum black catalyst were unsuccessful; a rapid initial absorption of hydrogen was observed but hydrogenation ceased after a few minutes. However, on distilling the olefins over copper chromite[3] with excess hydrogen, saturation proceeded smoothly, and after two such

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[1] From the master's thesis of L. H. Welsh, University of Maryland. 1935.

[2] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

[3] Adkins and Connor, *ibid.*, **53**, 1092 (1931).