hours. The solvent was then slowly distilled over a period of five hours. The residue was then refluxed with alcoholic potassium hydroxide for thirty minutes. It was extracted with ether, the solvent was removed and the residue was crystallized from ether and from dilute acetone, m. p. 169–171°.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2. Found: C, 79.4; H, 10.2.

On heating with acetic anhydride it gave a diacetate which was crystallized from dilute methanol, m. p. 121°.

Anal. Calcd. for $C_{25}H_{36}O_4$: C, 74.9; H, 9.1. Found: C, 74.6; H, 9.2.

A mixture of 50 mg. of $\Delta^{5,16}$-pregnadiendiol-3,20 in 20 cc. of ether and 20 cc. of methanol containing a few drops of acetic acid was shaken with 100 mg. of platinum oxide catalyst under a pressure of 45 pounds of hydrogen for one hour. The solution was filtered and the solvent was removed. The product was crystallized from acetone m. p. 192–194°. Mixed with *allo*-pregnanediol-3(β),20(β), m. p. 192–194°, it gave no depression in melting point.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.7; H, 11.3. Found: C, 78.5; H, 11.2.

Summary

1. Using methods previously developed a pregnanetriol-3(β),16,20(β), a pregnanetriol-3(α),16,20(β) and an *allo*-pregnanetriol-3(α),16,20(β) have been prepared from the pseudosapogenins. The last was not identical with *allo*-pregnanetriol from the urine of pregnant mares.

2. Desoxypseudosarsasapogenin acetate was converted to Δ^{16}-pregnenone-20.

3. α-Methylglutaric acid has been identified as the side-chain fragment arising from the hydrolysis of the oxidation products of pseudosapogenins.

4. $\Delta^{5,16}$-Pregnadienediol-3(β),20(β) and Δ^{16}-*allo*-pregnenediol-3(β),20(β) have been prepared.

STATE COLLEGE, PENNA. RECEIVED DECEMBER 19, 1940

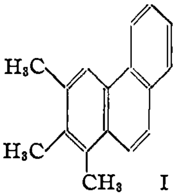
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Syntheses in the Phenanthrene and Triphenylene Series

BY LOUIS F. FIESER AND WILLIAM H. DAUDT

Following Cook's observation that 5,6-dimethyl-1,2-benzanthracene and 1,2,5,6-dibenzanthracene exhibit carcinogenic activity of about the same degree when applied to the skin of mice,[1] a number of ortho and peri dimethyl derivatives of anthracene, 1,2-benzanthracene, and chrysene have been investigated as possible models of higher condensed ring compounds of established carcinogenicity having an additional aromatic ring affixed at the points of attachment of the methyl groups.[2] The only prior investigation of models in the phenanthrene series is that of Hewett,[3] who synthesized 1,2,3,4-tetramethylphenanthrene for comparison with the highly potent carcinogen 9,10-dimethyl-1,2-benzanthracene.

The present work was taken up with the idea that 1,2,3-trimethylphenanthrene (I) would be of interest for comparison with the carcinogen 10-methyl-1,2-benzanthracene and that 2,3,4-trimethylphenanthrene might constitute a model of either 9-methyl-1,2-benzanthracene or 2-methyl-3,4-benzphenanthrene, both of which are known to be carcinogenic. Methods of synthesizing both hydrocarbons were found starting with *dl*-α,β-dimethylsuccinic anhydride, which was prepared from ethyl cyanoacetate and ethyl α-bromopropionate according to Bone and Sprankling.[4] The Friedel and Crafts reaction between this anhydride and naphthalene proceeded only poorly, but the Grignard synthesis gave very satisfactory results.



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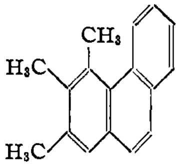

II

The condensation of α-naphthylmagnesium bromide and dimethylsuccinic anhydride afforded the keto acid III in yield comparable with the yields obtained in similar condensations with phthalic anhydride[5] and cyclopentane-1,2-dicarboxylic anhydride[6] and much superior to those

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(1) Cook and Haslewood, *J. Chem. Soc.*, 428 (1934); Barry, Cook, Haslewood, Hewett, Hieger and Kennaway, *Proc. Roy. Soc.*, **117B**, 318 (1935).

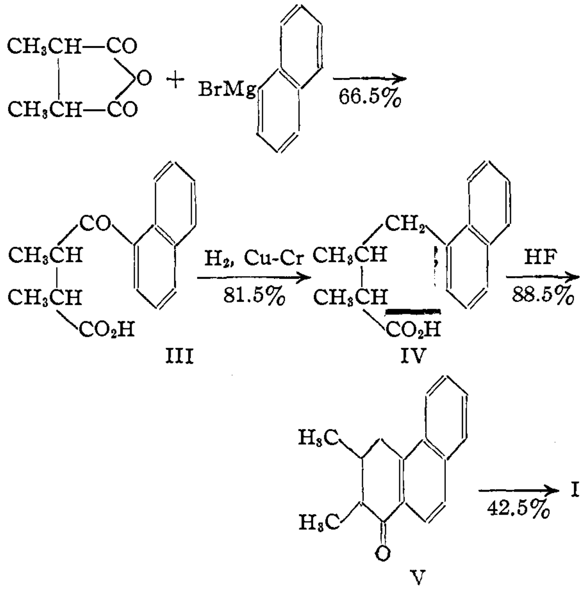
(2) Recent papers: Fieser and Webber, THIS JOURNAL, **62**, 1360 (1940); Newman, *ibid.*, **62**, 2295 (1940).

(3) Hewett, *J. Chem. Soc.*, 293 (1940); Hewett and Martin, *ibid.*, 1396 (1940).

(4) Bone and Sprankling, *ibid.*, **75**, 839 (1899). See also Böeseken, Schweizer and van der Want, *Rec. trav. chim.*, **31**, 92 (1912); Werner and Basyrin, *Ber.*, **46**, 3229 (1913); Verkade and Hartman, *Rec. trav. chim.*, **52**, 949 (1933).

(5) Weizmann, Bergmann and Bergmann, *J. Chem. Soc.*, 1367 (1935).

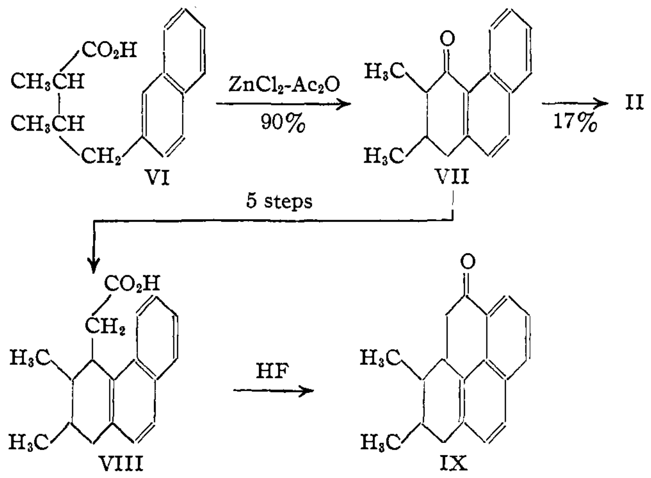
(6) Bergmann and Blum-Bergmann, THIS JOURNAL, **59**, 1572 (1937).



obtained with succinic or phenylsuccinic anhydride.[7] The acid apparently is produced in both possible diastereomeric forms, for the initial product melted over a considerable range and material of constant melting point was obtained in small amounts only after repeated crystallization. Since the isomerism disappears in the terminal stage of the synthesis, the total isomer mixture obtained in each intermediate step was used as such and a thorough separation was not attempted. The formation of diastereomers from an essentially homogeneous preparation of *dl*-α,β-dimethylsuccinic anhydride probably is the result of racemization of the keto acid through the enol form. Indeed a marked tendency to enolize was noted on attempted Fischer esterification of the acid, for this gave in place of the ester a crystalline enol lactone. Under comparable conditions unbranched β-aroylpropionic acids are esterified. Although the substance presumably is a β,γ-unsaturated γ-lactone, it does not give the characteristic Legal test.[8]

α,β-Dimethyl-β-(1-naphthoyl)-propionic acid (III) could not be reduced by the Clemmensen method or with zinc and alkali (even in the autoclave), and it formed no semicarbazone. The hindered carbonyl group was reduced very smoothly, however, by high-pressure hydrogenation of a neutral aqueous solution of the sodium salt[9] in the presence of copper chromite catalyst. The reaction stops abruptly after the consumption of two moles of hydrogen and the catalyst is not attacked, as it is when the free acid is hydrogenated in dioxane solution (green solution). Ring closure to the ketone V was accomplished smoothly with liquid hydrogen fluoride,[10] and Clemmensen reduction of the product, followed by dehydrogenation with palladium charcoal, gave the known 2,3-dimethylphenanthrene.[11] The crude carbinol obtained by the addition of methylmagnesium bromide to the ketone V was converted into 1,2,3-trimethylphenanthrene by heating it with palladium charcoal.[12] When the crude carbinol was heated at 200° without catalyst in order to effect dehydration, the reaction mixture was found to contain a considerable quantity of 1,2,3-trimethylphenanthrene, evidently produced as a result of a disproportionation.

In a second series β-naphthylmagnesium bromide was found to condense smoothly with *dl*-α,β-dimethylsuccinic anhydride (71.5% yield) to give a keto acid similar in properties to III. On hydrogenation as before this gave the acid VI in 91% yield. With this acid two directions of cyclization are possible, and when hydrogen fluoride was used the results of subsequent processing suggested that a significant amount of the linear isomer was present in addition to the hydrophenanthrene derivative VII. Since ring closure with zinc chloride catalyst in acetic acid-anhydride[13]



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(7) (a) Komppa and Rohrmann, *Ann.*, **509**, 259 (1934); (b) Weizmann, Blum-Bergmann and Bergmann, *J. Chem. Soc.*, 1370 (1935); (c) Bergmann and Blum-Bergmann, THIS JOURNAL, **59**, 1441 (1937); (d) Hill, Short and Stromberg, *J. Chem. Soc.*, 1619 (1937); (e) Fieser and Joshel, THIS JOURNAL, **61**, 2958 (1939).

(8) Jacobs and Hoffmann, *J. Biol. Chem.*, **67**, 333 (1926).

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

(10) Fieser and Hershberg, *ibid.*, **61**, 1272 (1939).

(11) (a) Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934); (b) Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935).

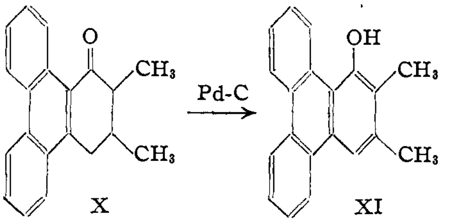
(12) Bachmann and Wilds, *ibid.*, **60**, 624 (1938).

(13) Fieser and Hershberg, *ibid.*, **59**, 1028 (1937).

has been found in other instances to be more favorable than the hydrogen fluoride method to the formation of angular products,[14] this method was employed, apparently with advantage, although because of the stereoisomerism the course of the reaction could be judged only indirectly by examining the final product obtained after Grignard addition, dehydration and dehydrogenation. In conducting this process another difficulty was encountered which seemed traceable to incomplete addition of the Grignard reagent to the highly hindered carbonyl group of the ketone VII. A useful expedient was found in subjecting the crude methyl carbinol to dehydration and passing a hexane solution of the product through a tower of alumina, when the unchanged ketone was retained on the adsorbent and effectively eliminated. 2,3,4-Trimethylphenanthrene was then easily obtained in a pure form by dehydrogenation over palladium.

Another synthetic use of the ketone VII was briefly investigated in preliminary experiments. By aluminum isopropoxide reduction, conversion to the chloride with hydrogen chloride in benzene, and application of the malonic ester synthesis the substance was converted into 2,3-dimethyl-1,2,3,4-tetrahydrophenanthrene-1-acetic acid (VIII). This was cyclized to the hydropyrene derivative IX (stereoisomer mixture), but at that point the work had to be discontinued.

The third series of experiments represents an extension of a previous study of triphenylene homologs.[7e] Application of the above synthetic operations to 9-phenanthrylmagnesium bromide gave the ketone X, from which 2,3-dimethyltriphenylene and 1,2,3-trimethyltriphenylene were obtained without difficulty. When the ketone X was heated with palladium charcoal in a sealed tube at 310°[7e,9] the substance was converted in part into 2,3-dimethyltriphenylene and in part into the phenol XI. The latter compound can be separated readily from the mixture by selective adsorption on alumina and elution with benzene-alcohol.



X XI

At an early stage of this work we considered the possibility of synthesizing 1,2,3-trimethylphenanthrene starting with the addition of dimethylmaleic anhydride to 1-propenylnaphthalene. However, no addition product could be obtained, the starting materials being recovered unchanged after being heated together even at elevated temperatures in a sealed tube. The reaction between 1-propenylnaphthalene and maleic anhydride was investigated for comparison and found to proceed readily at the temperature of the steam-bath.

Experimental Part[15]

α,β-Dimethylsuccinic anhydride was prepared on a large scale by the method of Bone and Sprankling.[4] A solution prepared from 70 g. of sodium and 750 g. of absolute ethanol was stirred mechanically while slowly running in 340 g. of ethyl cyanoacetate followed by 515 g. of ethyl α-bromopropionate, the latter reagent being added over a period of two hours. Two hours after the addition the bulk of the solvent was removed by distillation from the steam-bath and the mixture was poured into 5 l. of water and extracted with ether. Distillation of the product from a Claisen flask gave 510 g. (84%) of α-methyl-β-cyanosuccinate, b. p. 140–170° at 14 mm. This was added slowly to a solution from 55 g. of sodium and 450 cc. of absolute ethanol, and 400 g. of methyl iodide was then added slowly with mechanical stirring and ice cooling. After two hours the mixture was heated on the steam-bath for one hour and the solvent was then largely distilled and the product collected as above and distilled, giving 395 g. (73%) of methylated product, b. p. 150–160° at 17 mm. For hydrolysis 390 g. of the nitrile was refluxed overnight with 1500 cc. of concentrated hydrochloric acid, during which time a considerable amount of *dl*-α,β-dimethylsuccinic acid had separated. After cooling, 79 g. of *dl*-acid, m. p. 200–205°, was collected and concentration of the filtrate to 600 cc. afforded 63 g. of acid containing some of the *meso*-isomer (m. p. 163–180°). The filtrate was made alkaline with ammonia, treated with an aqueous solution of 110 g. of calcium chloride, and the precipitated calcium salt, after coagulation at the boiling point for one hour and cooling, was collected, suspended in water and treated with dilute hydrochloric acid. The solution, when concentrated and cooled, deposited 44 g. of the *meso*-acid, m. p. 112–115°; total yield of acids, 189 g. (75%). For conversion to the *dl*-anhydride, the different crops of stereoisomers were combined and the total acid mixture (186 g.) was treated with 275 g. of acetyl chloride and refluxed for one hour. Distillation at atmospheric pressure and redistillation of the fraction boiling at 225–240° gave 175 g. (79%) of *dl*-α,β-dimethylsuccinic anhydride, b. p. 234–237°, m. p. 50–70° (36% over-all yield from the bromo ester). Crystallization from absolute ether containing a small amount of acetyl chloride afforded 38 g. of material, m. p. 83–86°, which was

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[14] Fieser and Johnson, THIS JOURNAL, **61**, 1647 (1939); Fieser and Hershberg, *ibid.*, **62**, 49 (1940); compare Fieser and Seligman, *ibid.*, **60**, 170 (1938).

[15] All melting points are corrected.

suitable for use in the synthesis and 27 g., m. p. 75–80°; several recrystallizations were required to give completely pure *dl*-anhydride, m. p. 88–89°.

1,2,3-Trimethylphenanthrene

α,β-Dimethyl-β-(1-naphthoyl)-propionic Acid (III).—The Grignard reagent prepared from 35 g. of purified α-bromonaphthalene in 80 cc. of ether and 125 cc. of benzene was added under nitrogen with stirring during two hours to a suspension of 20 g. of *dl*-dimethylsuccinic anhydride in 250 cc. of refluxing ether. A light yellow complex separated. After refluxing for two hours longer the mixture was allowed to stand in the cold for at least one hour and the precipitate was then collected, washed with ether, and shaken in a separatory funnel with dilute ammonium chloride solution and ether. After standing for several hours for completion of the decomposition the layers were separated and the ethereal solution was washed with dilute acid and extracted four times with 10% sodium carbonate solution. After clarification with Norit the soda solution was run slowly into a stirred mixture of ice and excess hydrochloric acid. The granular precipitate of acid melted at 123–142° and weighed 26.6 g. (66.5%). One crystallization of this mixture of stereoisomers from benzene–ligroin gave 23.4 g. of small, colorless needles, m. p. 127–142°. Several crystallizations from dilute methanol afforded 19.3 g. of material melting at 144–147°, and on six additional crystallizations there was obtained an apparently pure substance of the constant m. p. 151.2–151.4°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.92; H, 6.22.

Attempts to prepare the semicarbazone were unsuccessful. The Friedel and Crafts method of preparation proved less satisfactory than that described. The reaction between the *dl*-anhydride (9 g.) and naphthalene was conducted in nitrobenzene solution in the presence of aluminum chloride and the acidic product was refluxed with methanol and sulfuric acid and the neutral fraction was distilled at 4 mm. (b. p. 200–215°) and saponified with 25% alcoholic sodium hydroxide. Crystallization afforded 3 g. of colorless acid mixture, m. p. 120–140°.

α,β - Dimethyl - γ - (1 - naphthyl) - Δ^{β} - crotonolactone.—A solution of 150 mg. of the keto acid (m. p. 151.2–151.4°) in 8 cc. of acetic acid containing a few drops of either acetic anhydride or acetyl chloride was saturated in the cold with hydrogen chloride and allowed to stand overnight. After evaporation of most of the solvent in vacuum the lactone was crystallized twice from benzene–ligroin, when it formed stout prisms, m. p. 96–97° (120 mg.). The same product (m. p. 94–96°) was obtained on refluxing the keto acid with methanol containing hydrogen chloride for four hours (second analysis).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.40, 80.58; H, 5.95, 6.07.

The lactone reduces Tollens' reagent rapidly but does not give the Legal test.[8]

α,β-Dimethyl-γ-(1-naphthyl)-butyric Acid (IV).—A solution of 6.75 g. of the keto acid in a slight excess of aqueous sodium hydroxide was rendered neutral to litmus by the addition of hydrochloric acid and shaken with 1 g. of copper chromite catalyst at an initial pressure of 1500–2500 lb. At 140° one mole of hydrogen was absorbed very rapidly and a second was consumed in five to ten hours. After clarification of the filtered solution with Norit it was run by drops with stirring into ice and acid. The precipitated acid was often gummy and tended to oil out on crystallization, but it proved to be entirely satisfactory for the next step; yield 5.2 g. (81.5%). A sample crystallized from hexane and then from dilute methanol melted at 102–106° and evidently is a mixture of diastereomers (a). Repeated recrystallization afforded a small amount of one of the pure racemates, m. p. 107.5–108.5° (b) while a second isomer of sharp melting point was obtained from the first mother liquors by cooling a ligroin solution in dry-ice–acetone. After recrystallization from dilute methanol this melted at 114–115° (c) and depressed the m. p. of the sample (b).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: (a) C, 79.01; H, 7.53. (b) C, 79.04; H, 7.34. (c)[16] C, 79.11; H, 7.46.

2,3 - Dimethyl - 1 - keto - 1,2,3,4 - tetrahydrophenanthrene (V).—A solution of 5.1 g. of the precipitated acid in 160 cc. of liquid hydrogen fluoride was allowed to stand overnight in a platinum vessel, the excess acid was evaporated and the residue was washed in benzene with dilute alkali and water and the neutral product collected and distilled at 3 mm. This gave 4.2 g. (88.5%) of a light yellow oil suitable for the next step. A portion of the material was obtained crystalline from ligroin, and after sublimation in vacuum and crystallization from methanol it formed colorless needles, m. p. 91–98° (mixture).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.63; H, 7.35.

A 0.5-g. sample of the oily ketone was reduced by the Clemmensen-Martin procedure and the resulting oil was heated with 10% palladium charcoal for one-half hour at 300–330°. The product distilled as a light yellow oil and this gave a picrate which, after several crystallizations from methanol and benzene–hexane formed bright yellow needles, m. p. 147.5–148.5°. This showed no depression when mixed with authentic **2,3-dimethylphenanthrene picrate**,[11b] m. p. 146–147°. The recovered hydrocarbon crystallized from petroleum ether in small plates, m. p. 79.2–79.7°, and was similarly identified as 2,3-dimethylphenanthrene.

1,2,3-Trimethylphenanthrene (I).—A solution of 3.9 g. of the oily ketone in 200 cc. of benzene was refluxed for sixteen hours with the Grignard reagent from 1.4 g. of magnesium and excess methyl bromide. The crude carbinol was collected as an oil, mixed with 0.3 g. of 10% palladium charcoal and heated slowly to 300° and then at 300–350° for one hour. The hydrocarbon was extracted with benzene and converted into the picrate which, after recrystallization, was obtained as bright orange needles, m. p. 187–188°; yield 2.8 g. (53%). After a further crystallization the picrate was decomposed with the use of an alumina adsorption tower and the hydrocarbon then crystallized from a concentrated solution of petroleum ether in the form of colorless prisms, m. p. 63.8–64.8°; yield 1.1 g. (42.5%).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.68; H, 7.40.

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[16] Microanalysis by Lyon Southworth.

The **trinitrobenzene derivative** crystallized from benzene–alcohol in light yellow needles, m. p. 200.7–201.5°.

In one experiment the crude carbinol (0.54 g.) was dehydrated by heating it at 200° and the product was sublimed at 17 mm. This failed to crystallize, but treatment with picric acid gave 0.41 g. (40%) of needles of the trimethylphenanthrene picrate indicating that a disproportionation of the intermediate dihydride had occurred.

2,3,4-Trimethylphenanthrene

α,β-Dimethyl-β-(2-naphthoyl)-propionic acid was obtained from β-naphthylmagnesium bromide and *dl*-α,β-dimethylsuccinic anhydride by the above procedure in 71% yield. The crude acid, m. p. 140–150°, was satisfactory for the succeeding steps. A sample recrystallized twice from dilute methanol afforded prisms, m. p. 149–153°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.93; H, 6.33.

The **enol lactone**, m. p. 126–127.5° (negative Legal test), was prepared as above. Treatment of the keto acid at room temperature with methanol saturated with hydrogen chloride gave the same product and not the methyl ester (m. p. 79.5–80°) described by Hewett.[3]

Anal.[16] Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.78; H, 5.86.

α,β-Dimethyl-γ-(2-naphthyl)-butyric acid (VI) was prepared by hydrogenation of the sodium or potassium salt of the keto acid in aqueous solution. The diastereomeric mixture was obtained in 91% yield as an oil satisfactory to use. About half of this was obtained as a solid from hexane, and crystallization from hexane and from methanol gave an apparently homogeneous racemate melting at 83–84°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.19; H, 7.46.

2,3 - Dimethyl - 4 - keto - 1,2,3,4 - tetrahydrophenanthrene (VII) (a) with Hydrogen Fluoride.—Cyclization of 1.2 g. of the acid with this reagent at room temperature gave after distillation of the neutral fraction 1.01 g. (91%) of a light yellow solid. A sample when crystallized from ligroin, sublimed, and crystallized from dilute methanol formed colorless needles, m. p. 81–84°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 86.06; H, 7.14.

The wide melting range may be due in part to the presence of some of the linear isomer. Reduction of a small sample of the ketone and dehydrogenation of the product gave 2,3-dimethylphenanthrene, isolated as the picrate (m. p. 146.5–148°) in low yield and only after several crystallizations.

(b) **With Zinc Chloride and Acetic Anhydride.**—When treated with the reagent in the usual way,[13] 1.20 g. of the acid gave, after distillation, 0.99 g. (90%) of ketone, m. p. 50–75°. Purification of a small sample of this material as above gave colorless needles apparently consisting principally of a single racemate, m. p. 93.5–95.5°, with slight previous softening (Found: C, 85.64; H, 7.38). 2,3-Dimethylphenanthrene (identified as picrate) was likewise obtained from the distilled ketone.

2,3,4-Trimethylphenanthrene (II).—Difficulties were encountered on applying to the distilled ketone samples prepared by methods (a) and (b) the procedure of Grignard addition and treatment of the crude carbinol with palladium charcoal. Hydrocarbon mixtures invariably resulted and in the case of the material from sample (a) the color of the nitro complexes was suggestive of the presence of anthracene derivatives. Thus a picrate mixture, m. p. 100–132°, was dark brown and a trinitrobenzene complex formed bright red needles, m. p. 140–152°. Fractionation of the latter derivative and decomposition of the complex with stannous chloride afforded a small amount of crude 2,3-dimethylphenanthrene, m. p. 67–74° (no depression). The appearance of this hydrocarbon suggested that the Grignard addition had been incomplete and the procedure was therefore modified to the extent of dehydrating the crude carbinol in a separate step and subjecting the product to a chromatographic adsorption process calculated to free the hydrocarbon fraction from any ketonic material present. The procedure was as follows.

The oily product from 2.88 g. of the distilled ketone preparation (b) and excess methylmagnesium bromide was heated at 200° to effect dehydration and the residue was distilled at 3 mm. and passed in hexane solution through a column of activated alumina. The hydrocarbon fraction recovered from the filtrate was an oil; yield 1.72 g. (60%). Dehydrogenation with palladium charcoal gave 0.9 g. of hydrocarbon mixture, m. p. 40–55°. On four crystallizations from methanol there was obtained 250 mg. (17%) of homogeneous 2,3,4-trimethylphenanthrene in the form of colorless needles, m. p. 62.8–63.8°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.51; H, 7.55.

The **picrate** formed bright orange-red needles, m. p. 113–114° from alcohol, and the **trinitrobenzene derivative** crystallized from benzene–alcohol in light yellow needles, m. p. 139–140°.

2,3 - Dimethyl - 4 - hydroxy - 1,2,3,4 - tetrahydrophenanthrene.—The ketone (VII) (1.9 g.) was refluxed for ten hours with a toluene solution (25 cc.) of the aluminum isopropoxide obtained from 1 g. of aluminum sheeting. The collected product was an oily solid from which 0.43 g. of crystalline material was obtained with benzene–hexane. Two crystallizations from ether–hexane gave colorless needles, m. p. 111–114.5°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.90; H, 8.02. Found: C, 84.79; H, 8.01.

On heating the crude product at 200° and then with palladium charcoal up to 350° there was obtained, in the form of the picrate, m. p. 144–146°, a hydrocarbon identified as 2,3-dimethylphenanthrene.

2,3 - Dimethyl - 1,2,3,4 - tetrahydrophenanthrene - 4-malonic Acid.—The total crude carbinol resulting from the reduction of 2.8 g. of the ketone was taken up in 75 cc. of benzene and the solution saturated with dry hydrogen chloride gas. The solvent was allowed to evaporate by standing overnight in an evaporating dish and the residue was dissolved in 15 cc. of benzene and added to a solution prepared from 0.5 g. of sodium in 15 cc. of absolute alcohol and 5.3 g. of diethyl malonate. The mixture was warmed slowly and then refluxed overnight. After evaporation of most of the solvent the material was refluxed for two hours with 25 cc. of 40% aqueous potassium hydroxide solution. On cooling and adding acetone a part of the malonic acid derivative separated in the form of the potassium salt; this was collected, the solution was clarified with Norit and acidified. The precipitated acid crystallized from benzene–acetone as colorless prisms, m. p. 188–190° with gas evolution (260 mg.).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.50; H, 6.66.

The alkaline mother liquor was diluted, washed with benzene, and acidified, giving 0.7 g. of crude acid as a brown solid.

2,3 - Dimethyl - 1,2,3,4 - tetrahydrophenanthrene - 4-acetic acid (VIII) was obtained by heating the purified malonic acid (120 mg.) for ten minutes at 200°. Two crystallizations from petroleum ether afforded a colorless isomer mixture, m. p. 110–123°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.51; H, 7.44.

3,4 - Dimethyl - 1 - keto - 1,2,2a,3,4,5 - hexahydropyrene (IX).—The crude malonic acid derivative (0.7 g.) was heated at 200° to effect decarboxylation and the residue transferred with benzene to a platinum vessel and treated with 70 g. of hydrogen fluoride (fifteen hours.) The product was taken up in benzene and the solution was washed with alkali and water, dried and diluted with hexane, when 160 mg. of a dark crystallizate was obtained. Sublimation and crystallization from benzene–alcohol gave 200 mg. of colorless plates in two crops, m. p. 204.5–206.5° and 197–202°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.42; H, 7.49.

Triphenylene Derivatives

α,β-Dimethyl-β(9-phenanthroyl)-propionic Acid.—From 16 g. of *dl*-α,β-dimethylsuccinic anhydride and the Grignard reagent from 46 g. of 9-bromophenanthrene there was obtained, after decomposition of the total reaction mixture with dilute acid and extraction of the acidic material with soda, 28.2 g. (74%) of crude keto acid. Crystallization from acetic acid and from benzene gave a fraction (5.2 g.) consisting largely of a single racemate, m. p. 170–171.5°, with slight previous softening.

Anal. Calcd. for $C_{28}H_{18}O_8$: C, 78.41; H, 5.92. Found: C, 78.59; H, 5.82.

This material afforded a **picrate** (fine yellow needles, m. p. 176–177°) and a **trinitrobenzene derivative** (nearly colorless needles, m. p. 188.5–189.2°). The enol **lactone**, prepared by treatment of the acid with either acetic acid and a few drops of acetyl chloride or with methanol and hydrogen chloride, formed stout prisms, m. p. 216–218°.

Anal.[16] Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.20; H, 6.03.

α,β-Dimethyl-γ-(9-phenanthryl)-butyric Acid.—High pressure hydrogenation of the keto acid in the form of the salt proceeded to an end-point with the absorption of two moles of hydrogen. The crude acid was obtained as an amorphous white solid in 88–93% yield. Crystallization from benzene–ligroin and from dilute methanol gave small needles of a mixture, m. p. 158–163°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.31; H, 6.98.

The crystallized acid gave a picrate (yellow needles) and a **trinitrobenzene derivative**, the latter after several recrystallizations melting at 174–175.5°.

2,3 - Dimethyl - 1 - keto - 1,2,3,4 - tetrahydrotriphenylene (X).—Cyclization of 12 g. of the amorphous acid with hydrogen fluoride and distillation of the neutral fraction gave 8.5 g. (71%) of a light yellow oil which partially solidified. A sample crystallized twice from benzene–ligroin (m. p. 119–130°), sublimed, and crystallized from ethanol formed colorless blades, m. p. 132–138°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.55; H, 6.57.

The ketone formed complexes with picric acid and trinitrobenzene.

1,2,3-Trimethyltriphenylene was prepared by the procedure of removing non-hydrocarbon material before dehydrogenation as described for 2,3,4-trimethylphenanthrene. After sublimation at 150° and 3 mm. and three crystallizations from benzene–alcohol the hydrocarbon was obtained as colorless needles, m. p. 109.8–110.6°; yield 0.25 g. (25%).

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.06; H, 6.81.

The **picrate** crystallized from benzene–alcohol in orange-red needles, m. p. 186–186.5°, and the **trinitrobenzene derivative** separated from benzene in fine, light yellow needles, m. p. 203.7–204.1°.

2,3-Dimethyl-1,2,3,4-tetrahydrotriphenylene.—The distilled ketone (1.28 g.) in 20 cc. of toluene was refluxed for three days with 50 g. of amalgamated zinc and 100 cc. of concentrated hydrochloric acid, added in portions. Vacuum distillation gave 1.15 g. (95%) of colorless product, m. p. 100–145°. The sample for analysis was crystallized once from ligroin, m. p. 158–167° (forms complexes with picric acid and trinitrobenzene, m. p. 154–158° and 158–160°).

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.86.

2,3-Trimethyltriphenylene.—The tetrahydride (1.10 g.) was heated gradually with 0.11 g. of 10% palladium charcoal to 300° and then for one-half hour at 300–325°. The distilled product was converted to the **picrate** which, when purified by crystallization from benzene–alcohol, formed orange needles, m. p. 210–211° (1.30 g.). The hydrocarbon was recovered by passing a benzene solution of the picrate through a tower of alumina. It crystallized from benzene–alcohol in long, colorless needles, m. p. 156.7–157.2°; yield 675 mg. (62%).

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.88; H, 6.40.

The **trinitrobenzene derivative** crystallized from benzene as light yellow needles, m. p. 237–237.7°.

2,3-Dimethyl-1-hydroxytriphenylene.—A mixture of 0.9 g. of the ketone and 0.1 g. of 10% palladium charcoal was heated in a sealed Pyrex tube at 300–310° for seven hours. The product was extracted with benzene and the solution passed through a column of activated alumina and Super-Cel (1:1). From the fluorescent filtrate there was obtained 200 mg. of light yellow needles of impure hydrocarbon; purification through the picrate gave 90 mg. of 2,3-dimethyltriphenylene, m. p. 156.2–157°, identified by mixed m. p. determination.

A yellow zone on the column was removed by elution with benzene–alcohol, and a crystalline yellow product obtained after concentrating the solution gave on sublimation 240 mg. of material, m. p. 167–168.5°, and 70 mg., m. p. 160–165°. The total product was converted to the **trinitrobenzene derivative**, which crystallized from benzene–alcohol in bright orange needles, m. p. 239–240°. Decomposition of the derivative in benzene–alcohol with stannous chloride and hydrochloric acid afforded colorless plates. On recrystallization from alcohol 250 mg. (26%) of colorless blades were obtained, m. p. 167.5–168.5°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.95; H, 5.96.

The substance dissolves only with difficulty in hot, dilute alkali. The sample darkened on storage and the melting point was depressed. The **picrate** crystallized from benzene–alcohol in bright red needles, m. p. 210.5–211.5°.

Addition of Maleic Anhydride to 1-Propenylnaphthalene.—A mixture of 14 g. of the hydrocarbon[17] and 35 g. of the anhydride was heated on the steam-bath for five hours, during which time the addition product crystallized from the melt. After washing with ether, 17.2 g. (77.5%) of white product, m. p. 261–263°, was obtained. Crystallization from acetic acid, ethyl acetate, and benzene–acetone afforded colorless needles, m. p. 271.8–272°.

Anal. Calcd. for $C_{17}H_{14}O_8$: C, 76.68; H, 5.28. Found: C, 76.33; H, 5.30.

Since the substance was not isomerized by being refluxed for five hours in acetic acid–anhydride saturated with hydrogen chloride,[18] it probably is **3-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-diçarboxylic anhydride**.

3-Methylphenanthrene-1,2-dicarboxylic anhydride was obtained in small amounts (10%) by heating the above product with two equivalents of sulfur. The tarry reaction mixture was extracted with acetic acid and the product sublimed and crystallized from chlorobenzene and from benzene, giving orange-yellow needles, m. p. 332–333°.

Anal. Calcd. for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.86; H. 4.11.

Summary

dl-α,β-Dimethylsuccinic anhydride condenses smoothly with the Grignard reagents from α- and β-bromonaphthalene and 9-bromophenanthrene to give the respective α,β-dimethyl-β-aroylpropionic acids in 66–74% yields. These keto acids were reduced to the γ-arylbutyric acids in excellent yield by hydrogenation over copper chromite catalyst in neutral aqueous solution. Cyclization gave intermediates from which the following new hydrocarbons were synthesized: 1,2,3-trimethylphenanthrene, 2,3,4 - trimethylphenanthrene, 2,3-dimethyltriphenylene, and 1,2,3-trimethyltriphenylene. The first two substances were desired as possible models of carcinogenic hydrocarbons of the 1,2-benzanthracene and 3,4-benzphenanthrene series.

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[17] Fieser and Hershberg, THIS JOURNAL, **60**, 1658 (1938).

[18] Cook and Warren, *J. Chem. Soc.*, 1318 (1937).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. X. The Vapor Phase Fluorination of Acetone

BY NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In recent papers,[1] we have discussed the vapor phase fluorination of organic gases over a copper gauze catalyst. It seemed very desirable, however, to extend the scope of this successful process, and to make it applicable to volatile organic liquids as well. This paper will deal with the results obtained by the fluorination of acetone, when the liquid sample was introduced into a heated reaction chamber, through a calibrated capillary.

Apparatus and Operation.—The new apparatus is illustrated to approximate scale in Fig. 1. The organic liquid A, under air pressure measured by B, entered the vertical electrically heated brass reaction chamber C through glass capillary D, which was connected by a mercury sealed slip-joint E. The sample volatilized at once, and the gas passed into the copper gauze packing at G, while the fluorine was led in through H, and entered the packing at I below G. The reaction took place smoothly, and the gaseous products passed out above, through J, while less volatile material was collected simultaneously below in K. The gases passed through two heated tubes filled with sodium fluoride, L and L′ and were condensed by liquid air or dry-ice in the trap M, which was protected from air and moisture at all times, by passing nitrogen either through O or the bubble counter P. In operation, with acetone, the reaction chamber was first heated to 60°, but the temperature rose considerably as the fluorination progressed. The sodium fluoride tubes were maintained at 95° continuously.

A number of runs were made under different conditions, and the lower boiling products from M separated into empirical cuts by distillation, using the Booth–Podbielniak fractionating unit. The results, expressed in liquid volume per cent. of the total condensate, and rounded off

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[1] Paper IX, THIS JOURNAL, **62**, 3302 (1940); see also VII, *ibid.*, **62**, 267 (1940).