downward distillation. Distillation was continued until no further volatile material evolved.

For those acids and ketones of boiling point above the decomposition temperature of the iron(II) carboxylates, the reflux apparatus was retained following cessation of the evolution of the hydrogen. The Ascarite tube was removed from the gas delivery train and refluxing was continued until evolution of carbon dioxide ceased. Usually 1 hr. sufficed for complete decarboxylation of the iron(II) carboxylate. At this point the flask was set for downward distillation and the crude ketone distilled from the reaction mixture.

The crude ketone was shaken with a saturated solution of sodium hydrogen carbonate to remove traces of unreacted acid, then dried with silica gel and redistilled, or recrystallized from ethanol, or ethanol and water, depending upon the properties of the product.

CORAL GABLES, FLA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

Erythrophleum Alkaloids. Synthesis of 1,2,8,10-Tetramethylphenanthrene[1]

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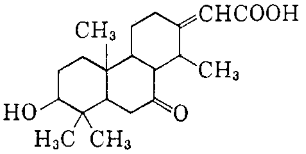
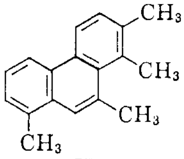
Received September 7, 1961

1,2,8,10-Tetramethylphenanthrene, the degradation product from cassaic acid that served to fix the location of the carbonyl group in the latter compound, has been synthesized. 7-Methyl-1-oxo-1,2,3,4-tetrahydronaphthalene, by reaction with methyl Grignard reagent followed by dehydration and hydrogenation, gave 1,7-dimethyl-1,2,3,4-tetrahydronaphthalene. Friedel-Crafts acetylation, Reformatsky condensation with ethyl 2-bromopropanoate, dehydration, and catalytic reduction afforded 2-methyl-3-(3′,5′-dimethyl-5′,6′,7′,8′-tetrahydro-2′-naphthyl)butanoic acid. After dehydrogenation to the corresponding naphthalene derivative, the side chain was extended by application of the Arndt-Eistert process. Cyclization of the resulting homolog gave 4-oxo-1,2,8,10-tetramethyl-1,2,3,4-tetrahydrophenanthrene, which on reduction followed by aromatization furnished the desired 1,2,8,10-tetramethylphenanthrene. The availability of this authentic synthetic material permitted direct comparisons to be made with, and so proved the structure of, the tetramethylphenanthrene obtained from cassaic acid.

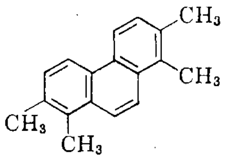
One of the hydrolysis products from cassaine, the major alkaloid from *Erythrophleum guinneense*, is cassaic acid (I). The tricyclic irregular diterpenoid skeleton of cassaic acid was inferred from degradation experiments[4,5] and was later firmly established by relating the material to vouacapenic acid.[6] The hydroxyl and carbonyl groups were at first placed provisionally as shown in formulation I.[5] Subsequently, confirmation of this assignment was obtained on the one hand by attaching a methyl group to the carbon atom originally part of the carbonyl group of cassaic acid (I) and aromatizing to produce 1,2,8,10-tetramethylphenanthrene (II) and, on the other hand, by attaching a methyl group to the carbon originally carrying the hydroxyl group and aromatizing to produce 1,2,7,8-tetramethylphenanthrene (III). As aromatization of cassaic acid derivatives to which no extra methyl group had been added gave 1,2,8-trimethylphenanthrene (IV),[4] the tetramethyl derivatives served to fix the locations of the two oxygen functions.[7] Although authentic 1,2,7,8-tetramethylphenanthrene (III) had been reported before[8] and fortunately was available for direct comparisons, the 1,2,8,10-tetramethyl derivative was unknown. Synthesis of the latter compound accordingly was necessary; and it is with this synthesis that the present paper is concerned.



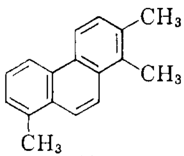
I



II



III



IV

The starting point was the tetralone V, which was prepared in three steps from toluene and succinic anhydride.[9,10] Methyl Grignard reagent

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[1] Abstracted from the Dissertation submitted by Subodh C. Chakravarti to the Graduate School of Boston University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, 1960.

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(4) *Cf.* G. Dalma in Chapter 36 of *The Alkaloids*, by R. H. F. Manske and H. L. Holmes, Vol. IV, Academic Press, New York, 1954; T. A. Henry, *The Plant Alkaloids*, 4th edition, Blakiston Company, Philadelphia, Pa., 1949, p. 725.

(5) L. G. Humber and W. I. Taylor, *J. Chem. Soc.*, 1044 (1955); R. Tondeur, Ph.D. thesis, Eidgen. Techn. Hochschule, Zurich, 1950.

(6) F. E. King, T. J. King, and J. M. Uprichard, *J. Chem. Soc.*, 3428 (1958).

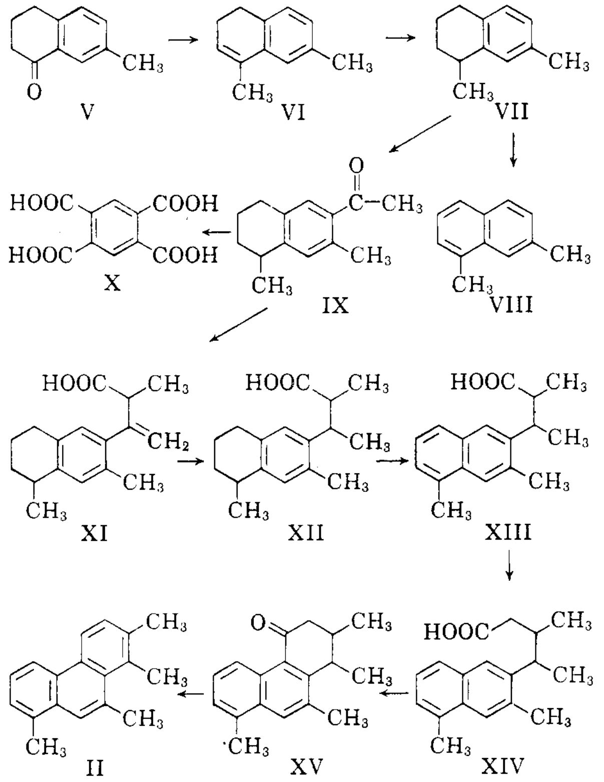
(7) W. J. Gensler and G. M. Sherman, *J. Am. Chem. Soc.*, **81**, 5217 (1959); also *cf.* V. P. Arya and D. W. Mathieson, *J. Chem. Soc.*, 3623 (1959).

(8) B. G. Engel, A. Ronco, K. Berse, Pl. A. Plattner, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1713 (1949).

(9) E. de Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

(10) E. L. Martin, *Org. Reactions*, **I**, 164 (1942).

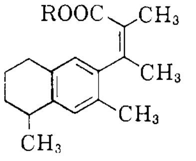
was added to tetralone V, and the resulting alcohol was directly dehydrated to give dihydronaphthalene VI. Catalytic hydrogenation over palladium at room temperature converted the unsaturated compound to 1,7-dimethyl-1,2,3,4-tetramethylnaphthalene (VII). An intense 12.36-μ absorption found for the unsaturated compound but not for the hydrogenated product corresponded to an out-of-plane vibration of vinyl hydrogen in a trisubstituted ethylene[11] and supported the endocyclic arrangement as in VI.[12] However, small amounts of the corresponding exocyclic isomer were not entirely excluded.

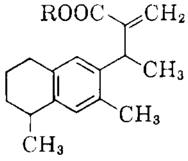


A side product in the catalytic hydrogenation of dihydronaphthalene VI to tetrahydronaphthalene VII was the fully aromatic 1,7-dimethylnaphthalene (VIII),[9] formed evidently by disproportionation.[12,13] The same naphthalene VIII was also obtained by dehydrogenating the tetrahydronaphthalene VII.

Acetylation of the tetrahydronaphthalene VII with acetyl chloride and aluminum chloride furnished 2-acetyl-3,5-dimethyl-5,6,7,8-tetrahydronaphthalene (IX) in high yield. Oxidation of the acetyl derivative to 1,2,4,5-benzenetetracarboxylic acid (X) confirmed the expected orientation. A Reformatsky condensation of the acetyl derivative IX with ethyl 2-bromopropanoate gave a product which was directly dehydrated and saponified to the unsaturated acid XI (80%).

Isomeric structures were considered for acid XI and its methyl ester, notably those with the ethylenic bond conjugated with the carboxyl group as in XIa or XIb. The unsaturated side chain in XIa and in XIb could assume a sterically unhindered conformation in which the double bond is coplanar with the carboxyl group. If this were true, an absorption maximum in the 220-mμ region would be expected.[14] However, since both acid XI and its ester show only ill-defined absorption maxima at 281 mμ, conjugation between ethylene and carboxyl groups is unlikely. Another remote possibility is that the entire side chain in XIa is coplanar with the aromatic ring. If this were true, the ultraviolet absorption curve would be expected to resemble that of 3-(1′,2′,3′,4′-tetrahydro-6′-naphthyl)acrylic acid and should show absorption maxima at 228, 235, and 290 mμ.[15] Accordingly, coplanar structure XIa is also unsatisfactory. In structure XI, too, a coplanar arrangement is unacceptable, as, for example, the observed absorption curve does not resemble that of 2-(*p*-tolyl)propene,[16] which has a maximum at 247 mμ and an inflection point near 290 mμ. Structure XI with the unsaturated side chain nonplanar and hence not conjugated with the benzene ring is the most reasonable choice. In 2-(*o*-tolyl)propene, for example, in which the isopropenyl group and the ring are in different planes, no absorption peaks appear between 220–320 mμ.[16,17] Scale models of XI support this assignment by exhibiting considerable crowding of groups in the planar but not in the nonplanar conformation. Peaks at 10.97 and 10.99 μ in the infrared absorption curves for butenoic acid XI and its ester support the structures with a terminal methylene group; this absorption is absent in butanoic acid XII.


XIa


XIb

Although catalytic hydrogenation of the ethylenic bond in acid XI over palladium in either alcohol or glacial acetic acid failed, hydrogenation

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[11] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1954.

[12] Cf. J. Jacques and H. B. Kagan, *Bull. soc. chim. France*, 128 (1956).

[13] Cf. R. P. Linstead and K. O. A. Michaelis, *J. Chem. Soc.*, 1134 (1940); E. A. Braude and R. P. Linstead, *J. Chem. Soc.*, 3544 (1954); E. A. Braude, R. P. Linstead, and P. Mitchell, *J. Chem. Soc.* 3578 (1954).

[14] A. T. Nielsen, *J. Org. Chem.*, 22, 1539 (1957).

[15] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York, 1951. Spectrum No. 73.

[16] M. J. Murray and W. S. Gallaway, *J. Am. Chem. Soc.*, 70, 3867 (1948).

[17] P. Ramart and J. Hoch, *Bull. soc. chim.*, [5], 5, 848 (1938).

over platinum gave the desired saturated acid XII in good yield.[18] Acid XII, a mixture of stereoisomers, was esterified and the ester was aromatized with sulfur. After several stages, naphthalene acid XIII was obtained as two partially purified fractions. A sharp melting isomer, isolated from the first of the two fractions examined, provided enough material to carry the synthesis to completion; accordingly, no attempt was made to isolate the second isomer of XIII from the other fraction.

Application of the Arndt-Eistert sequence transformed the crystalline acid XIII to its homolog XIV. Cyclization with liquid hydrogen fluoride led to the cyclic keto derivative XV (77%), which after treatment first with lithium aluminum hydride and then with palladium at 300° gave the desired 1,2,8,10 - tetramethylphenanthrene (II) (46%). The close agreement between the properties of the abovementioned degradation product from cassaic acid (I) and those of the synthetic material established the structure of the degradation product and therefore the location of the carbonyl group in cassaine.[7] The synthetic work of Turner and his colleagues[19] provided independent evidence in support to these findings.

The synthesis of 1,2,8,10-tetramethylphenanthrene adds another authentic tetramethylphenanthrene to the list of known isomers, which now includes 1,2,3,4- (m.p. 92–93°),[20] 1,2,3,8- (m.p. 96–97°),[21] 1,2,7,8- (m.p. 170–170.5°; 173°),[8,22] 1,2,8,10-(m.p. 109.5–110.5°), and 2,3,8,9-tetramethylphenanthrene (m.p. 106–107°).[23] Other reported tetramethylphenanthrenes about which some question may exist include the 1,2,6,8- (picrate m.p. 177°),[24] 1,4,5,10- (m.p. 85.8–86.4°),[25] 2,5,8,9- (m.p. 90°),[26] and 3,4,9,10-isomers (m.p. 115°).[27] An isomer of unknown structure has also been reported.[28]

EXPERIMENTAL[29]

1,7-Dimethyl-3,4-dihydronaphthalene (VI). The directions of Barnett and Sanders[9] were modified, so that aluminum chloride (7.2 moles) was added in portions to a stirred solution (held below 25°) of succinic anhydride (3.5 moles) and toluene (3.5 moles) in 1,2-dichloroethane solvent (1.2 l.) over a period of 6 hr. After an additional 2 hr. of stirring at 20°, the mixture was heated on the steam bath for 4 hr. Crystalline 3-(4′-methylbenzoyl)propanoic acid, m.p. 124–127°, was obtained in 82% yield. Clemmensen reduction of this material[10] gave 4-(4′-methylphenyl)butanoic acid, m.p. 59–60°, in 88% yield. Ring closure on a half-mole scale according to the general directions of Barnett and Sanders[9] furnished the methyltetralone V, m.p. 35–37°, in 78% yield. In the cyclization, using 85% sulfuric acid at 90–100° for 2.5 hr. was advantageous.

A solution of 0.33 mole of tetralone V in 70 ml. of ether was added at 0° by drops to 50 ml. of a stirred solution of Grignard reagent from 0.42 mole of methyl iodide and 0.4 mole of magnesium.[9] After an additional 1 hr. reflux period, the stirred mixture in an ice bath was treated with 100 ml. of cold 6*N* hydrochloric acid added dropwise followed by 50 ml. of concentrated hydrochloric acid. The aqueous layer was extracted with ether, and the combined ether solutions were washed with two portions of water, then with two portions of 10% sodium thiosulfate solution, and finally with water. The dried ether solution was concentrated, and the residue was fractionated through a vacuum-jacketed 25 cm.-Vigreux column. The clear water-white product (87%), n_D^{25} 1.5663, distilled at 68–73° (0.1– 0.35 mm.). A redistilled sample of the 1,7-dimethyl-3,4-dihydronaphthalene (VI) boiled at 70–72° (0.1–0.3 mm.) and showed n_D^{25} 1.5662.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.8; H, 9.0.

The neat material showed infrared absorption peaks at 11.24(w), 11.34(m), and 12.36(s)μ.

1,7-Dimethyl-1,2,3,4-tetrahydronaphthalene (VII). A mixture of 38.0 g. (0.24 mole) of 1,7-dimethyl-3,4-dihydronaphthalene (VI), n_D^{25} 1.5662, 1.85 g. of palladium (10%)-on-charcoal, and 265 ml. of purified absolute ethanol was stirred under an atmosphere of hydrogen at room temperature. The solvent and catalyst were presaturated with hydrogen. After 3.5 hr., when 63% of the calculated amount of hydrogen had been taken up, hydrogen absorption ceased. Catalyst and solvent were removed, and the pale yellow residue was distilled through a 25-cm. vacuum-jacketed Vigreux column. The desired colorless product, 1,7-dimethyl-1,2,3,4-tetrahydronaphthalene (VII), b.p. 54–56° (0.2 0.25 mm.), n_D^{25} 1.5302, weighed 30.0 g. (78%). The analytical sample, b.p. 55–57° (0.15–0.18 mm.), showed the same index of refraction. The boiling point reported before for the same material is 100° (6 mm.).[30]

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.2; H, 10.1.

The infrared spectrum of the neat liquid showed absorption at 12.48 μ but none at 12.36 μ. Three relatively weak absorption bands were also noted (carbon tetrachloride solution) in the order of increasing intensity at 11.18, 11.37, and 11.7 μ.

Colorless 1,7-dimethylnaphthalene (VIII) was obtained as a higher boiling fraction (5.1 g. or 14%), b.p. 55–59° (0.03–0.01 mm.) or 248–250° at atmospheric pressure, with n_D^{25}

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[18] L. H. Schwartzman and B. B. Corson, *J. Am. Chem. Soc.*, **76**, 781 (1954), observed a similar behavior with 2,6-dimethylstyrene.

[19] R. B. Turner, E. G. Herzog, R. B. Morin, and A. Riebel, *Tetrahedron Letters*, March, 1959, p. 7.

[20] C. L. Hewett and R. H. Martin, *J. Chem. Soc.*, 1396 (1940).

[21] J. C. Bardhan, R. N. Adhya, and K. C. Bhattacharyya, *J. Chem. Soc.*, 1346 (1956).

[22] E. Heilbronner, H. U. Däniker, and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 1723 (1949).

[23] W. Carruthers and J. D. Gray, *J. Chem. Soc.*, 2422 (1957).

[24] J. R. Hosking and C. W. Brandt, *Ber.*, **68**, 286 (1935).

[25] M. L. Mosby, *J. Org. Chem.*, **19**, 294 (1954).

[26] J. Colonge and A. Arsac, *Bull. soc. chim. France*, 445 (1954).

[27] F. Bergmann and A. Weizmann, *J. Org. Chem.*, **11**, 592 (1946).

[28] L. Ruzicka, L. V. Engel, and W. H. Fischer, *Helv. Chim. Acta*, **21**, 364 (1938).

[29] Melting points and boiling points are uncorrected. Ultraviolet absorption spectra were determined with a Beckman-DU (manual) or a DK-1 (recording) spectrophotometer. Infrared spectra were determined with Perkin-Elmer single-beam (12-C) or double-beam (21) spectrophotometers. Wherever decolorizing carbon is called for, Norit was used. Elementary analyses were performed by Carol K. Fitz, 115 Lexington Avenue, Needham Heights, Mass., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Theoretical values were taken from H. Gysel, *Tables of Percentage Composition of Organic Compounds*, Verlag Birkhäuser, Basel, 1951.

[30] S. M. Mukherji, O. P. Vig, S. Singh, and N. K. Bhattacharyya, *J. Org. Chem.*, **18**, 1499 (1953).

1.5954–1.5958. The boiling point reported before is 258°[9] or 117–120° (17 mm.).[30]

1,7-Dimethylnaphthalene (VIII). (a) *From hydrogenation of 1,7-dimethyl-3,4-dihydronaphthalene* (VI). The 1,7-dimethylnaphthalene described above was converted to its picrate by mixing an alcohol solution of the material (0.2 g. in 1 ml.) with a cold saturated solution (5 ml.) of picric acid in alcohol. The voluminous yellow precipitate was washed with and then crystallized from anhydrous ether. The picrate showed m.p. 118–119°; mixed with picric acid, the picrate melted at 85–100°. The picrate of 1,7-dimethylnaphthalene has been reported with m.p. 120°[9] and m.p. 120–121°.[30]

(b) *By aromatization of 1,7-dimethyl-1,2,3,4-tetrahydronaphthalene* (VII). A mixture of tetrahydronaphthalene VII (2.0 g., 0.13 mole) and 10% palladium-on-charcoal (1.8 g.) in a flask provided with a condenser was heated in a metal bath. The temperature was held at 280–300° for 12 hr. and then at 300–320° for 2 hr. The contents of the flask were treated several times with boiling ether, and the combined ether solutions after drying with sodium sulfate were stripped of solvent at 100° under water pump vacuum. The dark oily residue in 15 ml. of petroleum ether (b.p. 40–60°) was placed on a column of Fisher Adsorption Alumina (30 g.). Then approximately 250 ml. of a 1:1 mixture of petroleum ether–benzene was passed through the column. After removing solvent at 100° from the combined eluates, 1.1 g. of pale yellow 1,7-dimethylnaphthalene was obtained. The picrate, recrystallized from ethanol, melted at 118–120°. A mixture with the material described above melted at 118–119°.

2-Acetyl-3,5-dimethyl-5,6,7,8-tetrahydronaphthalene (IX).[31] A 3-necked flask was fitted with a stirrer and a condenser cooled with a solid-carbon dioxide mixture. Redistilled 1,7-dimethyl-1,2,3,4-tetrahydronaphthalene (23.0 g. or 0.14 mole) was added followed by acetyl chloride (13.4 g. or 0.17 mole) purified by distillation from calcium carbonate and, after cooling the flask to 0°, by 150 ml. of carbon disulfide purified by distillation from phosphorus pentoxide. Powdered, reagent grade aluminum chloride (22.7 g. or 0.17 mole) was placed in a dry Erlenmeyer flask, which was then attached to the reaction flask with a short length of wide thin-walled rubber tubing. The aluminum chloride was added in small portions to the stirred mixture over a period of 1 hr. The reaction temperature was not allowed to go above 10°. After the dark brown mixture was stirred at room temperature for 3 hr., it was boiled for 1 hr.

The dark red reaction mixture, cooled to 5° in an ice-salt bath, was treated with 200 g. of crushed ice and 100 ml. of ice-cold concentrated hydrochloric acid. Much hydrogen chloride was evolved. After carbon disulfide was distilled from the mixture, the residual material was extracted with three 300-ml. portions of ether. Most of the brown color was removed when the ether extract was shaken with three 20-ml. portions of 5% sodium hydroxide solution. The ether extract was shaken with several portions of water to remove all traces of sodium hydroxide and then was dried with sodium sulfate. After solvent was removed, the residue was fractionated through a 25-cm. vacuum-jacketed Vigreux column. The desired acetyl derivative IX (26.7 g.; 94%) distilled at 114–117° (0.1–0.25 mm.) and showed n_D^{25} 1.5510. A sample redistilled for analysis had b.p. 115–117° (0.05–0.1 mm.) and n_D^{25} 1.5514.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.0; H, 9.0.

2-Acetyl-3,5-dimethyl-5,6,7,8-tetrahydronaphthalene (IX) as a $3.5 \times 10^{-5}M$ solution in 95% alcohol showed ultraviolet absorption maxima at 216 mμ (log ε 4.37), 256 (4.06), and 299 (3.28). The infrared absorption spectrum of either the neat material or a 10% solution in carbon tetrachloride showed a strong carbonyl peak at 5.94 μ.

The 2,4-dinitrophenylhydrazone was recrystallized from absolute alcohol–ethyl acetate and then from absolute alcohol. The orange-red needles melted at 155–156°.

Anal. Calcd. for $C_{20}H_{22}O_4N_4$: C, 62.81; H, 5.80; N, 14.65. Found: C, 6.28; H, 5.7; N, 14.7.

Pyromellitic Acid (X) *from 2-acetyl-3,5-dimethyl-5,6,7,8-tetrahydronaphthalene* (IX). A mixture of 3.8 ml. of nitric acid (52%) and 0.60 g. of 2-acetyl-3,5-dimethyl-5,6,7,8-tetrahydronaphthalene (IX) sealed in a 2 × 60 cm. Carius tube was heated in an electric oven. The temperature was raised gradually to 200°, held at 200–210° for 8 hr, and then allowed to drop to room temperature.

The bottom half of the tube was cooled in Dry Ice–acetone (better in liquid nitrogen) for about 1 hr. before the tube was opened. Proper precautions should be exercised as considerable pressure builds up. The contents of the tube were transferred to an open vessel with the help of some distilled water and evaporated on the steam bath. The residual gummy solid, on crystallization from water (decolorizing carbon was used), gave 0.45 g. of pale yellow crystals melting on the block at 255–265°. A second crystallization (decolorizing carbon) gave white prisms, which after drying at 105° for 2 hr. melted on the block at 270–271°. The capillary melting point, determined by heating the sample rapidly to within 10° of the melting point and then at a rate of 4° per min., was 262–264°. After the material resolidified, remelting was observed at 274–276°. A sample of authentic pyromellitic acid dihydrate, prepared by oxidation of 1,2,4,5-tetramethylbenzene,[32] melted at 264–266° and, after solidification, at 273–275°. A mixture melted at 264–266° and after resolidification at 278–279°.

2-Methyl-3-(3′,5′-dimethyl-5′,6′,7′,8′-tetrahydro-2′-naphthyl)-3-butenoic acid (XI). The following procedure was based on the general directions for the Reformatsky reaction described by Bachmann, Cole, and Wilds.[33] Granular zinc, after treatment with dilute hydrochloric acid, was washed thoroughly with water, acetone, and ether and then dried in vacuo at 110°. Pure ether and thiophene-free benzene, both dried over sodium wire, were used as solvent. The apparatus, a 3 necked round bottomed flask with a cold-finger Dry Ice condenser, dropping funnel, and magnetic stirring bar, was carefully dried before assembly. With dry nitrogen in the flask, 8.0 g. of zinc (0.12 g.-atom), 7.95 g. (0.040 mole) of freshly distilled 2-acetyl-3,5-dimethyltetrahydronaphthalene (IX), and 15.8 g. (0.090 mole) of dry distilled ethyl 2-bromopropanoate were mixed with 25 ml. of ether and 15 ml. of benzene. The mixture to which 0.2 g. of iodine was added was heated and stirred. After 10 min., the iodine color faded and vigorous boiling began. The mixture was allowed to boil first without and then with external heat. More zinc (8.0 g. or 0.12 g.-atom) with a few crystals of iodine was added in four portions at intervals of 40 min. More ethyl 2-bromopropanoate (15.0 g. or 0.08 mole) was introduced 2 hr. after the start of the reaction.

After a total reaction period of 4 hr., the reaction mixture, chilled to 5°, was treated with 150 ml. of ice-cold 5% hydrochloric acid. Filtration removed 6 g. of unused zinc.

The aqueous layer was extracted with three portions of benzene, and the combined organic layers washed in succession with several portions of 10% ammonium hydroxide, water, 10% aqueous sodium thiosulfate, and finally water. The solution, dried with sodium sulfate, was distilled on the steam bath first at atmospheric pressure to remove solvent and then under reduced pressure (3–4 min.) to remove other low boiling materials.

The viscous, dark brown residue (18 g.) of crude hydroxy

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(31) *Cf.* E. A. Coulson, *J. Chem. Soc.*, 77 (1935); L. F. Fieser, *Experiments in Organic Chemistry*, 3rd edition, D. C. Heath and Company, Boston, Mass., 1955.

(32) O. Jacobsen, *Ber.*, 17, 2516 (1884); W. H. Mills, *J. Chem. Soc.*, 101, 2191 (1912).

(33) W. E. Bachmann, W. Cole, and A. L. Wilds, *J. Am. Chem. Soc.*, **62**, 824 (1940).

ester with 25 ml. of benzene and 6.0 g (0.05 mole) of phosphorus pentoxide was held at the boiling point for 2 hr.[34] The reaction mixture was filtered and the solids rinsed with two portions of benzene. After solution in water, this residue was further extracted with ether. The combined ether and benzene solutions were washed twice with 10% aqueous ammonia and twice with water. The organic layer was dried with sodium sulfate, and low boiling materials were removed by distillation under water-pump pressures. Further distillation of the yellow viscous residual oil (17 g.) through a short Claisen head gave 11.9 g. of partially purified ethyl ester of the desired butenoic acid XI, b.p. 66–105° (0.0025 mm.). This yellow viscous ester showed intense absorption at 5.76 μ, a weak absorption peak at 6.11 μ, and one at 10.97 μ.

To saponify the ester, its solution with 15% methanolic potassium hydroxide (20 ml.) was boiled for 3 hr. After solvent was removed by distillation, 100 ml. of water was added and the cooled alkaline mixture extracted with several portions of ether. The aqueous layer was treated at the boiling point with decolorizing carbon, filtered, and then cooled. Acidification with 2*N* hydrochloric acid produced a white solid, which was extracted with ether. The ether solution was washed with water, dried with sodium sulfate, and all solvent removed under vacuum. The residue was redissolved in dilute potassium hydroxide, reprecipitated, and isolated as before. The faintly yellow viscous residue (8.2 g., 79%) was taken as a mixture of isomers of 2-methyl-3-(3′,5′-dimethyl-5′,6′,7′,8′-tetrahydro-2′-naphthyl)-3-butenoic acid XI.

In four similar preparations, product was obtained in 79–81% yield. Calcd. for $C_{17}H_{22}O_2$: neut. equiv., 258.3. Found: 256.8–262.7.

The product decolorized bromine in carbon tetrachloride immediately and decolorized permanganate solution rapidly. The ultraviolet absorption spectrum of a $3.5 \times 10^{-5}M$ solution in 95% alcohol showed a poorly defined maximum at 281 mμ (log ε 3.13). An 8% solution in carbon tetrachloride showed absorption maxima at the 3μ region as well as at 5.88(s), 6.11(v.w), and 10.97μ (w).

When acetyl derivative IX, ethyl 2-bromopropanoate, and zinc in the molar ratios 1:1:1, 1:1:2, or 1:2:2 were allowed to react in boiling benzene for several hours, and the mixture processed as before, the yield of desired product XI was 0–5% and the recovery of unchanged acetyl derivative IX was 90–95%.

Methyl 2-methyl-3-(3′,5′-dimethyl-5′,6′,7′,8′-tetrahydro-2′-naphthyl)-3-butenoate. An ice-cold solution of butenoic acid XI (0.30 g., 1.2 mmoles) in 5 ml. of anhydrous ether was treated with dry ethereal diazomethame (excess) prepared from 1 g. of *N*-nitroso-*N*-methylurea, and the mixture was allowed to stand overnight in the cold. Volatile materials were removed at reduced pressures at room temperature, and the ethereal solution of the residue washed first with two small portions of 10% aqueous sodium bicarbonate and then with water until the washings were neutral to litmus. After drying the ether solution with sodium sulfate, all material volatile at 100° under aspirator pressures was removed.

The partially purified ester of the butenoic acid was obtained as a viscous oil (0.30 g.). A $4.7 \times 10^{-5}M$ ethanol (95%) solution had an ultraviolet absorption maximum, almost a shoulder, at 281 mμ (log ε 3.23). This ester as a 10% solution in carbon tetrachloride showed absorption peaks at 3.23 (w), 5.76–5.82 (s), 6.11 (w), and 10.99 μ (m).

2-Methyl-3-(3′,5′-dimethyl-5′,6′,7′,8′-tetrahydro-2′-naphthyl)butanoic acid (XII). A solution of the butenoic acid XI (26 g., 0.10 mole) in glacial acetic acid (75 ml.) containing 0.26 g. of platinum oxide was shaken at room temperature in an atmosphere of hydrogen at 46 lb. When hydrogen absorption leveled off, more catalyst (0.27 g.) was added and the hydrogenation continued. Finally, a third portion of catalyst (0.52 g.) was introduced, and hydrogenation again resumed. The total pressure drop of 8 lb. observed over a period of more than 14 hr. corresponded to an absorption of approximately 0.1 mole of hydrogen.

The catalyst was removed and washed with hot acetic acid, and the combined filtrate and washings were concentrated by distillation under reduced pressure. The high boiling residue, dissolved in 100 ml. of 10% sodium hydroxide solution, was treated with decolorizing carbon, and the clear solution then acidified with 2*N* hydrochloric acid. The resulting precipitate was taken up in ether, and the ether solution was washed thoroughly with water and then dried with sodium sulfate. Complete removal of all material volatile at 100° at 30 mm. pressure left a viscous oil (25.4 g.; 97%), a mixture of stereoisomers of the desired 2-methyl-3-(3′,5′-dimethyl-5′,6′,7′,8′ - tetrahydro - 2′ - naphthyl)butanoic acid (XII).

The product failed to decolorize a 5% solution of bromine in carbon tetrachloride instantaneously and failed to decolorize permanganate solution for as long as 5 min. The neutralization equivalent calculated for $C_{17}H_{24}O_2$ (XII) is 260.4; the value observed was 262.3. In 11% carbon tetrachloride solution, the product showed absorption at 3–3.75 (with a sharp peak at 3.41) and 5.87 μ. No peak appeared at 10.97 μ, and the weak absorption peak present in the starting material at 6.11 μ was replaced by a shoulder.

2-Methyl-3-(3′,5′-dimethyl-2′-naphthyl)butanoic acid (XIII). An ice-cold solution of the butanoic acid XII (25.0 g., 0.096 mole) in 20 ml. of anhydrous ether was treated with a dry ether solution of diazomethane from 16 g. of *N*-nitroso-*N*-methylurea. After the mixture had stood in the icebox overnight, a few drops of glacial acetic acid were added. The colorless solution, after extraction with several portions of 10% sodium carbonate solution and washing with water, was dried with sodium sulfate. Complete removal of ether left 26.0 g. (98%) of the oily methyl ester of butanoic acid XII.

A mixture of this methyl ester (25.0 g., 0.090 mole) with sublimed sulfur (5.84 g., 0.18 mole) was heated under a condenser for 1.5 hr. at 220–240° and then for 0.5 hr. at 250–260°. Evolution of hydrogen sulfide, marked at first, could no longer be detected at the end of this period. Distillation of the dark reaction mixture through a Claisen head afforded 22.0 g. of red dehydrogenation product, b.p. 140–160° (0.01–0.05 mm).

This material was exposed to the action of 100 ml. of boiling 10% methanolic potassium hydroxide for 4 hr. The alkaline mixture, concentrated to about a fourth of its original volume, was diluted with 250 ml. of water, and washed with ether. The ether was washed with small portions of water, which was combined with the aqueous solution. The combined alkaline solutions were treated with decolorizing carbon, and the clear solution was acidified with dilute hydrochloric acid. The precipitated product was extracted with ether. The ethereal solution was washed free of mineral acid with water, dried with sodium sulfate, and stripped of all volatile material to give 2-methyl-3-(3′,5′-dimethyl-2′-naphthyl)butanoic acid XIII as a yellow solid weighing 20.0 g (85%).

The crude product was methylated with diazomethane by following essentially the same procedure as described above for the esterification of butanoic acid XII. The brown viscous ester (21.0 g.) of the naphthalene acid XIII was dissolved in 75 ml. of petroleum ether, b.p. 30–60°, and placed on a column of Merck acid–washed activated alumina (430 g.; 4 × 34 cm.). The column was eluted first with a total of 3100 ml. of petroleum ether. With the exception of the first 0.51 g. of emerging material which appeared to be extraneous matter and was discarded, all the petroleum ether eluate fractions were combined. Removal of all solvent left 10.4 g. of fraction-A as a colorless viscous oil.

Further elution with 1700 ml. of petroleum ether–benzene

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[34] Cf. G. A. R. Kon and K. S. Nargund, *J. Chem. Soc.*, 2461 (1932).

(3:1 by volume) removed 7.7 g. of product. Elution with 1700 ml. of petroleum ether–benzene (3:2 by volume) furnished an additional 1.7 g. As the last fraction showed the same infrared absorption curve as the 7.7 g. fraction, both were combined and labeled fraction B. The infrared absorption curve of fraction B in showing little or no absorption at 8.9 μ differed from that of fraction A, which had a band here.

The recovery of chromatographed material was 19.8 g. or 95%.

Most of fraction B (9.0 g.) was saponified essentially as already described above for the crude dehydrogenation ester. The acid product when rubbed under petroleum ether was transformed into a white solid, which after three cyrstallizations from hexane–petroleum ether furnished 2.8 g. of pure butanoic acid XIII, as clusters of plates, m.p. 130.5–132.5°. Reworking the various mother liquors gave more of the same crystalline acid (2.9 g.), m.p. 130.5–132.5°, so that the total yield of this isomer was 25%. The analytical sample after drying at 110° in vacuum over phosphorus pentoxide showed m.p. 131.5–132.5°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C,79.65; H,7.86; neut. equiv., 256.3. Found: C,79.8; H,8.0; neut. equiv., 255.8.

The infrared absorption curve of this acid XIII in 3% carbon tetrachloride solution showed an intense peak at 5.87 μ. The ultraviolet absorption curve (0.6×10^{-5} to 80×10^{-5} M in 95% ethanol) showed a series of distinctive features as follows: λ_{max} 324 mμ (log ϵ 2.36), 318 (2.52), 296(3.60), 287 (3.77), 276.5(3.74), 268 sh (3.60), 257 sh (3.39), 231.5 (5.03), 229 sh (4.98). The reported ultraviolet absorption curve for 2,3,5-trimethylnaphthalene in hexane[35] resembles the one determined here for acid XIII.

3-Methyl-4-(3′,5′-dimethyl-2′-naphthyl)pentanoic acid (XIV). The general procedure of Bachmann and Edgerton[36] was applied in converting butanoic acid XIII to its homolog XIV.

A cold solution of carefully dried, pure 2-methyl-3-(3′,5′-dimethyl-2-naphthyl)butanoic acid (XIII) (1.28 g.; 4.7 mmoles) in absolute ether (10 ml.) was added to an ice-cold solution of 4 drops of anhydrous pyridine and 1.1 ml. (15 mmoles) of purified thionyl chloride in 10 ml. of absolute ether. The reaction flask, protected from atmospheric moisture by a drying tube, was held in a bath at 5° for 1 hr. and then at room temperature for 1 hr.

All volatile material was removed at room temperature under reduced pressure. Pure benzene (10 ml.), dried over sodium wire, was added, and the volatile material removed. Another 10-ml. portion of benzene was added and completely removed. The residual solid acid chloride, dissolved in 25 ml. of cold anhydrous ether, was decanted carefully through a plug of glasswool into a stirred ice-cold solution of dry diazomethane (20 mmole) in 60 ml. of ether. The last traces of acid chloride were collected and added to the diazomethane solution with the help of two 10-ml. portions of ether.

After standing at 0–5° for 2 hr. and then at 20° for 2 hr., the yellow reaction mixture was stripped of all volatile material by exposure at room temperature to a water pump vacuum. The residual yellow diazo ketone in 25 ml. of anhydrous methanol was brought to 50° in a flask fitted with a condenser. The warm, magnetically stirred solution was treated with a slurry of 0.5 g. of freshly prepared silver oxide[37] in anhydrous methanol. Immediate evolution of gas was noted. The stirred mixture at 60–70° was treated with a second portion of silver oxide (0.25 g.) and 10 min. later with a third portion. The reaction was allowed to proceed for a total of 1.5 hr.

Solids were removed for the hot mixture and were rinsed with hot methanol. The combined solutions were concentrated, 15 ml. of 15% methanolic potassium hydroxide was added, and the alkaline mixture boiled for 16 hr.

Water (50 ml.) was added, and the solution was concentrated to a quarter of its volume and diluted with 25 ml. of water. After clarification with decolorizing carbon, the solution was acidified with ice-cold dilute nitric acid. The acid mixture was extracted thoroughly with ether, and the ether solution was washed twice with water and then dried over sodium sulfate. Removal of all ether left 1.38 g of crude product XIV.

A solution of this product in 50 ml. of dilute sodium bicarbonate solution was washed with several small volumes of ether and then acidified with 10% nitric acid. The precipitated product was collected in ether, and the ether solution was washed with water, dried over sodium sulfate, and finally distilled to remove solvent. When the dark brown, viscous residue (1.3 g.) was rubbed under cold petroleum ether, a solid formed. Several recrystallizations from *n*-hexane–petroleum ether (including a treatment with decolorizing carbon) gave rectangular prisms (52% yield) of pure 3-methyl-4-(3′,5′-dimethyl-2′-naphthyl)pentanoic acid (XIV), m.p. 100–101.5°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20; neut. equiv., 270.4. Found: C, 79.9; H, 8.2; neut. equiv., 271.5.

The product XIV, as a 2.3% solution in carbon tetrachloride, showed a strong absorption band at 5.87 μ. The ultraviolet absorption curve taken in 95% alcohol (0.7×10^{-5} to $90 \times 10^{-5}M$ solution) closely resembled that of the the butanoic acid precursor XIII. The absorption maxima for pentanoic acid XIV appeared at 324 mμ (log ϵ 2.34), 319(2.48), 296(3.58), 286(3.74), 276(3.72), 267(3.61), 257 (3.47), 232(4.97), and 228(4.92).

4-Oxo-1,2,8,10-tetramethyl-1,2,3,4-tetrahydrophenanthrene (XV).[38] The brown solution of 0.70 g (2.6 mmoles) of naphthylpentanoic acid XIV in ice-cold liquid hydrogen fluoride (25 ml.) in a polyethylene bottle was shaken occasionally during a period of 45 min. Hydrogen fluoride was removed in a stream of air, and the ethereal solution of the brown residue was shaken with 25 ml. of 20% aqueous potassium carbonate. The aqueous extract was washed with two portions of ether, and the combined ether solutions were washed with water to remove all carbonate and then dried over sodium sulfate. Removal of all solvent left 0.65 g. of residue, which was crystallized from petroleum ether (b.p. 30–60°) to give 0.53 g. of pale yellow crystalline product, m.p. 82–84°. Further purification was effected by passing a solution of the product in petroleum ether through a column of activated alumina (2 g., Fisher Adsorption Alumina). Elution was completed with fresh petroleum ether. Recrystallization from the same solvent gave beautiful white needles (0.50 g., 77%) of 4-oxo-1,2,8,10-tetramethyl-1,2,3,4-tetrahydrophenanthrene (XV), m.p. 83.5–85°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.75; H, 8.05.

The infrared absorption spectrum of the keto compound XV (carbon tetrachloride solution) showed intense peaks at 5.98 and 6.25 μ. The ultraviolet absorption curve of a $1.6 \times 10^{-5}M$ alcohol (95%) solution, in showing maxima at 336 mμ (broad) (log ϵ 3.59), 256 (4.26), and 220 (4.68), resembled that of 4-oxo-6,7,10-trimethyl-1,2,3,4-tetrahydrophenanthrene.[23]

The 2,4-dinitrophenylhydrazone of keto compound XV, after two crystallizations from ethanol–ethyl acetate, melted at 270–272°.

1,2,8,10-Tetramethylphenanthrene (II). A solution of carefully dried 4-oxo-1,2,8,10-tetramethyl-1,2,3,4-tetrahydrophenanthrene (XV: 0.505 g., 2.0 mmoles) in 10 ml. of anhydrous ether was added by drops to a magnetically stirred ice-cold slurry of 0.60 g. (16 mmoles) of lithium aluminum hydride with 80 ml. of anhydrous ether. After a 14-hr. reaction period at reflux temperature, the mixture was cooled

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(35) R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934).

(36) W. E. Bachmann and R. O. Edgerton, *J. Am. Chem. Soc.*, **62**, 2219 (1940).

(37) W. E. Bachmann and W. S. Struve, *Org. Reactions*, **I**, 38 (1942).

(38) Cf. W. S. Johnson, *Org. Reactions*, **II**, 157 (1944).

in an ice bath and was treated *carefully* with 20 ml. of water added dropwise. Ice-cold 1:1 hydrochloric acid (50 ml.) was added followed by a few drops of concentrated hydrochloric acid. The ether layer was removed, and the clear aqueous phase was extracted several times with ether. The combined ether solutions were washed with portions of water until the washings were neutral and were then dried over sodium sulfate. Complete removal of solvent left 0.49 g. (96%) of crude 4-hydrox-1,2,8,10-tetramethyl-1,2,3,4-tetrahydrophenanthrene. No absorption was evident at 5.98 μ; hydroxylic absorption was evident at 3.0 μ.

This crude material (0.48 g., 1.9 mmoles) was mixed with 0.28 g. of 10% palladium-on-charcoal (American Platinum Works) in a 20-ml. test tube fitted with an air condenser. The mixture was held in a bath at 280–290° for 1 hr. and then at 300–310° for 0.5 hr. The dehydrogenation mixture was extracted with several portions of anhydrous ether, and material that did not dissolve was rejected. Removal of all solvent gave 0.42 g. of partially crystalline product II.

A solution of the crude material in 40 ml. of petroleum ether (Reagent, b.p. 30–60°) followed by 100 ml. of the same solvent was passed through a 13 × 1 cm. column of activated alumina (Fisher Adsorption Alumina, 80–200 mesh; 9 g.). Evaporation of solvent from the emergent solution left 0.39 g. of pale yellow, waxy needles. Repetition of the cromatographic process yelded 0.35 g. of colorless product. Two crystallizations from methanol gave tiny white needles (0.21 g.; 46%) of 1,2,8,10-tetramethylphenanthrene (II), m.p. 108–110.5°. The sample prepared for analysis by another crystallization melted at 109.5–110.5°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.44; H. 7.86.

The ultraviolet absorption spectrum of 1,2,8,10-tetramethylphenanthrene (II) as a 0.1×10^{-4} to $8 \times 10^{-4}M$ alcohol (95%) solution showed the following maxima: 358 mμ (log ϵ 2.36), 351 (1.55), 342 (2.55), 336 sh (2.11), 311 (4.18), 298 (4.15), 286 sh. (4.16), 264 (4.81), 257 sh (4.74), 228 sh (4.33), 217.3 (4.61). The ultraviolet absorption curve matched the one observed for the same phenanthrene obtained as a derivative of cassaic acid.[7]

Three derivatives of 1,2,8,10-tetramehylphenanthrene (II) were prepared. According to the general directions of Vogel,[39] 30 mg. of the phenanthrene was combined with 28 mg. of 1,3,5-trinitrobenzene in absolute ethanol to give a bright yellow precipitate. Recrystallizations, once from absolute ethanol and twice from absolute ethanol-chloroform, furnished the trinitrobenzene derivative of 1,2,8,10-tetramethylphenanthrene (II) as bright yellow needles, m.p. 164–165°.

Anal. Calcd. for $C_{24}H_{21}O_6N_3$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.54; H, 4.67; N, 9.25.

The picrate derivative was prepared[39] by allowing a solution of 20 mg. of phenanthrene II and 25 mg. of picric acid in 4.5 ml. of 95% alcohol to stand at room temperature. Filtration afforded orange-red needles of the desired picrate, which was washed with a few drops of cold alcohol and then dried for two days in vacuo over phosphorus pentoxide. The melting point of the picrate was 141.5–142.5°.

Anal. Calcd. for $C_{24}H_{21}O_7N_3$: C, 62.20; H, 4.57; N, 9.07. Found: C, 62.48; H, 4.70; N, 8.91.

The trinitrofluorenone derivative was prepared[40] by allowing a solution of 24 mg. of 1,2,8,10-tetramethylphenanthrene (II) and 32 mg. of 2,4,7-trinitrofluorenone in a small volume of absolute ethanol to stand at room temperature for 0.5 hours. The precipitated deep orange-red solid was collected, washed with a few drops of cold absolute ethanol, and dried. Two crystallizations of the product from anhydrous benzene-ethanol gave the desired derivative in the form of dark orange-red clusters of needles melting at 166–167°.

Anal. Calcd. for $C_{31}H_{23}O_7N_3$: C, 67.75; H, 4.22; N, 7.65. Found: C, 67.89; H, 4.29; N, 7.74.

Interestingly, when the trinitrofluorenone derivative was brought out of *dilute* solution, the color of the deposited crystals was a much lighter orange. However, the melting point was the same (166–168°), and the melting point of a mixture (166–167°) of the two different colored materials was not depressed.

Acknowledgment. This work was aided by a grant from the Greater Boston Chapter of the Massachusetts Heart Association, for which we are grateful. S. C. C. acknowledges with appreciation receipt of a Fulbright Scholarship during the period 1955–1959; he also thanks the Department of Education, Government of West Bengal, India, for granting him study leave.

BOSTON 15, MASS.

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[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Syntheses of 3-Fluoro- and 4'-Fluoro-9,10-dimethyl-1,2-benzanthracene[1]

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Received October 4, 1961

The syntheses of 9,10-dimethyl-1,2-benzanthracene and of 4'-fluoro- and 3-fluoro-9,10-dimethyl-1,2-benzanthracenes are described.

The reasons for synthesis of fluoro derivatives of 9,10-dimethyl-1,2-benzanthracene for studies on carcinogenic activity have been presented.[2] In this paper a modified synthesis of 9,10-dimethyl-1,2-benzanthracene[3–7] is described and the syntheses

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[1] This work was supported by a grant from the National Institutes of Health.

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