ether, the ether extract washed with water, and then extracted with three 250-cc. portions of 5% sodium carbonate solution. The combined sodium carbonate extracts were neutralized with hydrochloric acid, heated to 70–80°, treated with charcoal, filtered and acidified. The crude α-phenoxy-p-hydroxycinnamic acid was obtained in a yield of 26 g. (40%) melting at 236–240°. Recrystallized for analysis from aqueous methyl alcohol, m. p. 245–246°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.70. Found: C, 70.26; H, 4.43.

B. A mixture of 48 g. of anhydrous potassium α-phenoxyacetate, 33 g. of p-hydroxybenzaldehyde and 100 cc. of acetic anhydride was heated for ten hours at 150°.[7] The reaction mixture was worked up as described under (A) and there was obtained 19 g. (30%) of the crude cinnamic acid melting at 224–229°. Recrystallized from dilute methyl alcohol, giving 13.4 g., m. p. 240–242°.

II. **α-Phenylmercapto-p-hydroxycinnamic Acid.** A.—This compound was prepared as described for the corresponding oxygen analog using 16.8 g. (0.1 mole) of phenylthioglycolic acid, 12.2 g. (0.1 mole) of p-hydroxybenzaldehyde, 10 g. (0.1 mole) of triethylamine and 100 cc. of acetic anhydride. The crude α-phenylmercapto-p-hydroxycinnamic acid was obtained in a yield of 10 g. (37%) melting at 206–209°. An analytical sample was recrystallized from acetone and water, m. p 211.5–213.5°.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.15; H, 4.45. Found: C, 66.50; H, 4.39.

B. Condensed for thirty-six hours at 100–110°, 51.5 g. (0.25 mole) of anhydrous potassium α-phenylthioglycolate, 30.5 g. (0.25 mole) of p-hydroxybenzaldehyde, and 200 cc. of acetic anhydride. The reaction product was worked up as described under I(A), crude yield 42 g. (61%), m. p. 202–206°. Recrystallization from acetone and water gave a product melting at 209–211°.

III. **α-Phenoxy-β-(p-hydroxyphenyl)-propionic Acid.**—To a solution of 40 g. of α-phenoxy-p-hydroxycinnamic acid in one liter of 1% sodium hydroxide, there was added in 50-g. portions 400 g. of 5% sodium amalgam. Before each addition of sodium amalgam, the solution was made almost neutral with dilute acetic acid. The aqueous solution was decanted from the mercury, filtered through Supercel and acidified after cooling. The crude reduction product amounted to 31 g. and melted at 165.5–166.5°; recrystallized from aqueous acetone, m. p. 169–170°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.74; H, 5.47. Found: C, 69.54; H, 5.10.

IV. **α-Phenylmercapto-β-(p-hydroxyphenyl)-propionic Acid.**—Ten grams of the unsaturated compound II was reduced as described for the oxygen analog. A crude yield of 6 g. was obtained melting at 118–119°; recrystallized from dilute alcohol, m. p. 126–127°.

Anal Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.97; H, 5.27.

V. **α-Phenoxycinnamic Acid.**—A mixture of 95 g. (0.5 mole) of anhydrous potassium phenoxyacetate, 53 g. (0.5 mole) of freshly distilled benzaldehyde and 400 cc. of acetic anhydride was heated with stirring at 105–115° for forty-eight hours. The reaction mixture was then cautiously decomposed with water and the crude α-phenoxycinnamic acid filtered, yield 41 g. (34%), m. p. 150–157°. The substituted cinnamic acid was purified by treatment with hot water which removed 10 g. of cinnamic acid, m. p. and mixed m. p. 129–130°. The pure α-phenoxycinnamic acid was obtained in a yield of 26 g. melting at 183.8–184.5° after recrystallization from aqueous alcohol, literature m. p. 179–180°.[2]

VI. **α-Phenylmercaptocinnamic Acid.**—Forty-eight and five-tenth grams (0.25 mole) of anhydrous sodium phenyl thioglycolate and 26.5 g. (0.25 mole) of benzaldehyde in 100 cc. of acetic anhydride were condensed as described for the corresponding oxygen compound. The crude acid was purified by recrystallization from aqueous alcohol and was obtained in a yield of 22 g. melting at 130–132°. The analytical sample which was also obtained by a recrystallization from aqueous alcohol melted at 143–144°.

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72. Found: C, 70.05; H, 5.11.

Acknowledgment.—The authors wish to express their appreciation to Miss Hilda Hankin for her assistance.

Summary

The Perkin condensation of phenoxyacetic acid and phenylthioglycolic acid with benzaldehyde and p-hydroxybenzaldehyde is reported. The reaction was carried out with the alkali metal salts as well as with the free acid in the presence of triethylamine.

The hydrogenation of the resulting cinnamic acids to the propionic acids was accomplished with sodium amalgam in dilute aqueous alkali.

BLOOMFIELD, N. J. RECEIVED JULY 11, 1947

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[7] These are the reaction conditions described by Oglialoro. Compare with those of preparation IIB and V.

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

The Synthesis and Optical Resolution of 4,5,8-Trimethyl-1-phenanthrylacetic Acid[1]

BY MELVIN S. NEWMAN AND ALLEN S. HUSSEY

In a previous publication[2] it was pointed out that there is considerable interference between the methyl groups in any compound of the 4,5-dimethylphenanthrene type. Since compounds of this type have been prepared previously[2] and the preparation of additional examples is herein described, the question of how the methyl groups are situated in space is of interest. Three possibilities may be considered: (1) the methyl groups lie bent away from each other but in the same plane as the aromatic rings; (2) the aromatic rings are distorted in some way; (3) the methyl groups are bent out of the plane of the aromatic rings.

In this paper we report on the synthesis of 1,4,5-trimethylphenanthrene, VI, and 4,5,8-trimethyl-1-phenanthrylacetic acid, VIII, and on the resolution of the acid VIII.[3] The first alternative

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[1] Most of the material herein presented is taken from the Ph.D. thesis of A. S. H. at O. S. U., March, 1946. Completing experiments on the resolution were carried out by A. S. H. at Northwestern University and by M. S. N. at O. S. U.

[2] Newman, THIS JOURNAL, **62**, 2295 (1940), note references 14–18.

[3] Newman and Hussey, *ibid.*, **69**, 978 (1947).

(above) is ruled out by the successful resolution of VIII. Of the second and third alternatives, we prefer the latter because of the ultraviolet absorption spectra of VI, VIII and phenanthrene (see Fig. 1). If the aromatic rings were distorted enough to produce the optical activity observed, the absorption curves for VIII and VI (which have similar features) would be expected to differ more from that of phenanthrene.

The optical activity herein reported, therefore, is due to the fact that the methyl groups in the four and five positions are not located in the same plane as the aromatic rings but on alternate sides. For convenience in future discussions, it is proposed to refer to isomerism arising from this feature as **optical isomerism of the 4,5-phenanthrene type.** It is interesting to compare this isomerization type with that of the biphenyls which owe their optical activity to the fact that the aromatic rings are non-coplanar.[4]

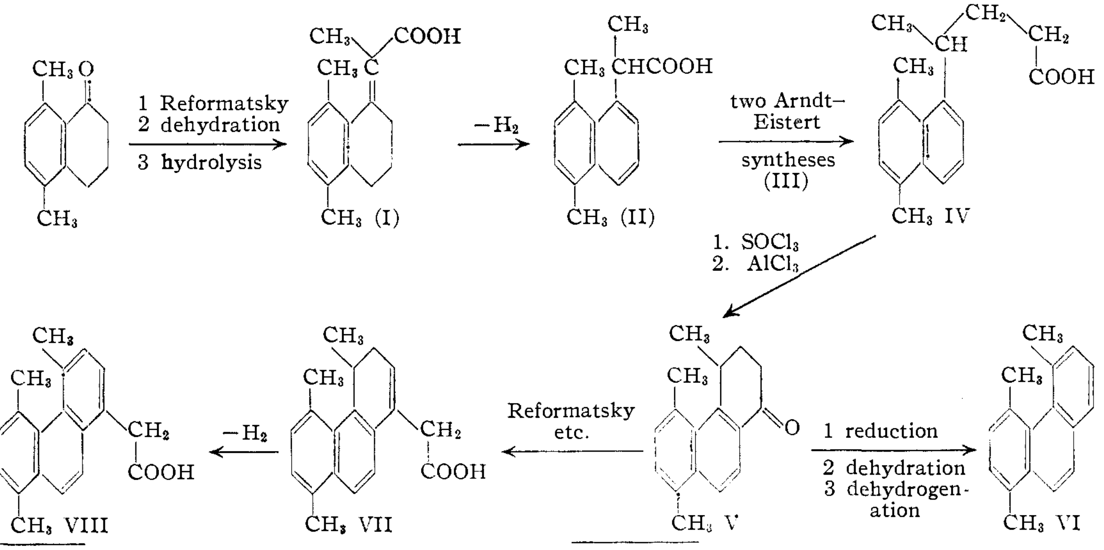
The requirements for optical isomerism of the 4,5-phenanthrene type are more simple than those for the biphenyl type. It is only necessary to have in the four and five positions of a phenanthrene nucleus two groups which have effective volumes large enough to prevent rapid slipping past a position of coplanarity with the aromatic plane. The optical antipodes in a simple case, namely, 4,5-dimethylphenanthrene, are shown and the synthetic approach to the compounds mentioned herein is outlined.

Three isomeric unsaturated acids, I, were isolated from the products of the Reformatsky reaction between 5,8-dimethyl-1-tetralone and ethyl α-bromopropionate. These forms undoubtedly correspond to the *cis–trans* geometric isomers of I and to the isomer of I which has the double bond in the ring. One form proved extremely difficult to esterify and is probably the isomer which has the carboxyl group *cis* to the 8-methyl group. It is interesting to note that a considerable amount of ethyl α-propionylpropionate was obtained as a by-product from this Reformatsky reaction.[5]

Dehydrogenation of the easily formed esters of the unsaturated acids, I, proved difficult to accomplish in high yield. On heating with sulfur considerable cleavage to ethyl propionate and 1,4-dimethylnaphthalene occurred. When dehydrogenation over a palladium-on-charcoal catalyst was attempted only about 30% of the theoretical amount of hydrogen was evolved. Although some cleavage took place the desired aromatic acid, II, was obtained (after hydrolysis) in 55% yield. This yield is made possible by disproportionation of the dihydro ester. It is remarkable that this result was obtained by heating at 300° for only twenty minutes.

The conversation of II to the diazoketone by the Arndt–Eistert method went smoothly, but attempts to convert this substance into the acid III, its ester, or amide by the recommended procedures[6] were unsuccessful. However, by using ethyl instead of methyl alcohol the desired ester was obtained in good yield.

Because of the difficulties met in this Arndt–Eistert reaction, an attempt was made to prepare



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[4] For a complete discussion of biphenyl isomerism see Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 343 et seq.

[5] This finding will be discussed in a later paper.

[6] Bachmann and Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 47–53.

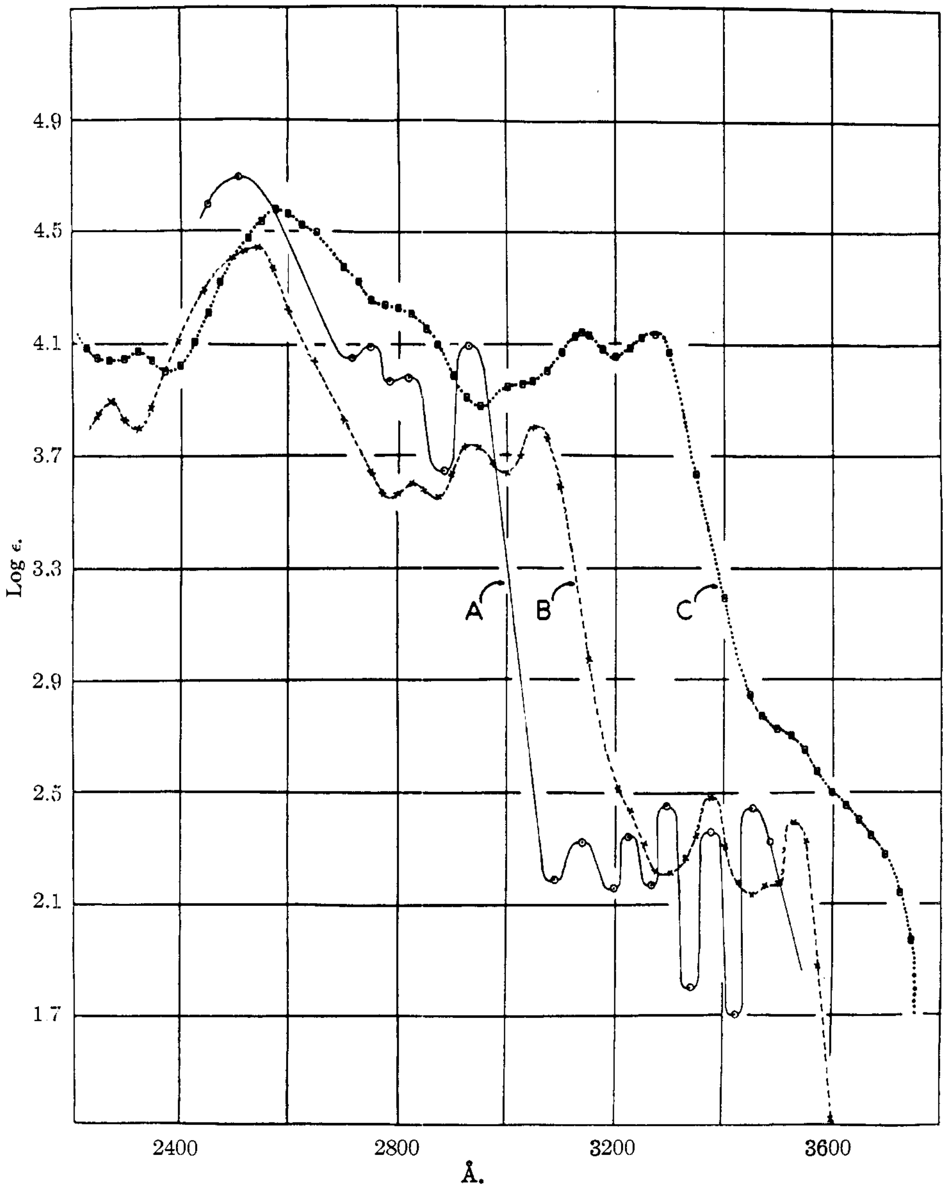

Fig. 1.—Absorption spectra: (A) phenanthrene, (B) 1,4,5-trimethylphenanthrene and (C) 4,5,8-trimethyl-1-phenanthrylacetic acid.

α-(5,8-dimethyl-1-naphthyl)-propionaldehyde by a Rosenmund[7] reduction of the acid chloride of II. Although hydrogen chloride was produced rapidly in high yield, the aldehyde was easily decarbonylated at the temperature of the reaction[8] to produce a hydrocarbon which was probably 1,4-dimethyl-8-ethylnaphthalene.

The remaining steps in the syntheses went well and need no comment. As a by-product in the final dehydrogenation of the ester of VII, a small amount of a second acid was obtained. This second acid is formed at the expense of VIII by loss of two hydrogens when the temperature for dehydrogenation is too high or when the reaction is prolonged unnecessarily. We believe this acid to be 8-methyl-4,5-dihydro-1-pyrenylacetic acid but further work is required to establish its structure without doubt.

The resolution of VIII was accomplished by recrystallization of the brucine salt. However, since both the salt and the acid racemize fairly rapidly in solution[9] at room temperature, the recrystallizations must be carried out quickly. For this reason we believe we have not achieved maximum resolution. However, for the theoretical

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[7] Rosenmund, *Ber.*, **54**, 425 (1921); Hershberg and Cason, "Organic Syntheses," **21**, 84 (1941).

[8] Compare Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943); Newman and O'Leary, *ibid.*, **68**, 258 (1946).

[9] This behavior is similar to that observed with some biphenyl compounds. For example, see Yuan and Adams, *ibid.*, **54**, 2966 (1932).

implications this is unimportant since the demonstration of optical activity suffices.

Experimental[10]

α-(5,8-Dimethyl-3,4-dihydro-1-naphthyl)-propionic Acid and Isomers.—Ethyl α-bromopropionate, 100 g. in all, zinc, 500 g. in all, and 43.5 g. (0.25 mole) of 5,8-dimethyl-1-tetralone, prepared in 68% over-all yield from pure *p*-xylene,[11] in 300 cc. each of ether and benzene reacted according to the general Reformatsky procedures developed by Bachmann[12] and co-workers. After hydrolysis the entire reaction product was heated to effect dehydration, vacuum distilled, saponified, and separated into neutral and acid fractions. From the former was recovered about 20% of ketone. The acid fraction was esterified with ethanol using benzene to aid in driving to completion; yet, after forty-eight hours, about 5 to 6% of the acid fraction remained unchanged. This acid (presumably the isomer of I containing the carboxyl groups *cis* to the 8-methyl group) was recrystallized from petroleum ether, b. p. 90–99° (Skellysolve C), to a melting point of 165.6–167.4°. The other isomers of I, obtained by saponification of a portion of distilled esters above described, melted at 114.6–115.4° (from petroleum ether, b. p. 35–40°, Skellysolve F) and 140.8–142.2° (from Skellysolve C). All combinations of the three isomers gave depressions of melting point. The 142° isomer formed about 65% of the mixture.

Anal.[d] Calcd. for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: (115° isomer) C, 78.4, 78.7; H, 8.0, 8.0; (142° isomer) C, 78.6, 78.5; H, 7.5, 7.9; (167° isomer) C, 78.1, 78.4; H, 8.0, 7.8.

The ethyl esters were obtained as a clear viscous liquid, b. p. 180–184° at 12 mm., $n^{25}D$ 1.5390, in 71% yield (87% based on ketone consumed).

Anal.[a] Calcd. for $C_{17}H_{22}O_2$: C, 79.0; H, 8.6. Found: C, 79.0, 78.7; H, 8.4, 8.4.

The semicarbazone of 5,8-dimethyl-1-tetralone was prepared and melted at 226.5–227.5° dec.

Anal.[a] Calcd. for $C_{13}H_{17}ON_3$: N, 18.2. Found: N, 18.5, 18.4.

α-5,8-Dimethyl-1-naphthylpropionic Acid, II. (a) **Dehydrogenation with Sulfur.**—Heating of 10.00 g. of ethyl α-5,8-dimethyl-3,4-dihydro-1-naphthylpropionate with 1.24 g. of sulfur at 195–200° for four hours followed by vacuum distillation and saponification afforded 4.40 g. of crude acid and 2.47 g. of neutral material. Fractional crystallization of the acid from Skellysolve C gave 2.44 g. of II, m. p. 134.5–136.5°. An analytical sample melted at 137.8–138.6°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 79.0; H, 7.0. Found[b]: C, 79.1, 78.9; H, 7.0, 7.0.

The neutral material, b. p. 265–267°, was identified as 1,4-dimethylnaphthalene by means of its picrate,[13] m. p. 141–143° (Fisher block, uncor.). A small amount of volatile material distilled from the reaction flask during dehydrogenation and was identified as ethyl propionate by its boiling point, 96–97°, and by formation of *p*-bromophenacyl propionate, m. p., and mixed m. p. with an authentic sample, 60–62°, from the acid formed on hydrolysis.[14]

(b) **Dehydrogenation over Palladium-on-Charcoal.**[15]—Four samples of ester totaling 108.7 g. were placed in four flasks connected to a common azotometer. To each flask was added 0.15 g. of 5% catalyst and the temperature was brought rapidly to 300°. Within twenty minutes 3.15 l. (30%) of hydrogen had been collected. After distillation under reduced pressure followed by saponification, 3.3 g. of 1,4-dimethylnaphthalene and 89.6 g. of crude acid were obtained. Crystallization of the acid fraction from Skellysolve C yielded 52% of II, m. p. 136.0–137.2°. Fractional distillation of the ethyl esters of the remaining acid afforded 20.0 g. of ethyl α-(5,8-dimethyl-1,2,3,4-tetrahydro-1-naphthyl)-propionate, b. p. 129–130° at 3 mm., $n^{25}D$ 1.5248.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.4; H, 9.3. Found[e]: C, 78.1, 78.1; H, 9.2, 9.2.

From the highest boiling (135–140° at 2 mm.) fraction of the esters there was obtained after hydrolysis an additional 3.1 g. of II, making a total yield of 55%.

1,4-Dimethyl-8-ethylnaphthalene.—A stream of dry hydrogen was passed through a well-stirred mixture at 160–170° of 3.5 g. of palladium-on-barium sulfate catalyst, one drop of sulfur-quinoline poison and 24.3 g. of the acid chloride of II in 150 cc. of purified *p*-cymene. After one hour 92% of the theoretical amount of hydrogen chloride had been collected. Suitable procedure allowed the isolation of about 60% of an oil, b. p. 116–119° at 1.5 mm., $n^{25}D$ 1.6108, but no further characterization was attempted.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.2; H, 8.8. Found[b]: C, 90.9; H, 8.5.

β-(5,8-Dimethyl-1-naphthyl)-butyric Acid, III.—Freshly distilled acid chloride (b. p. 149–51° at 0.3 mm.), from 30.0 g. of II was converted to the diazoketone by the action of diazomethane from 48 g. of nitrosomethylurea.[16] The pale yellow diazoketone was obtained in a crystalline state. The rearrangement of the diazoketone was carried out at 50° in 400 cc. of 95% ethanol by the addition of a slurry of freshly precipitated silver oxide in ethanol in portions as needed to maintain the evolution of nitrogen at a rate greater than 3 cc. per minute. After two hours 95% of the nitrogen had been evolved. After refluxing for two hours the wine-colored solution was filtered and the filtrate saponified. Fractional crystallization of the crude acid from Skellysolve C gave 17.8 g. (56%) of III melting above 132°. An analytical sample melted at 135.4–136.4° and depressed the melting point of II when mixed with it.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5; neut. eq., 242. Found[c]: C, 79.1, 79.0; H, 7.7, 7.7; neut. eq. 244.

γ-(5,8-Dimethyl-1-naphthyl)-valeric Acid, IV.—The acid chloride from 20.0 g. of III was converted to the diazoketone which was rearranged with silver oxide in 95% ethanol as above described. Ninety-eight per cent. of the theoretical amount of nitrogen was evolved within forty minutes. The product was saponified and the acid fractionally crystallized from Skellysolve C. The yield of colorless acid IV melting above 102° was 15.9 g. (75%); an analytical sample melted at 103.8–104.8°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.9; neut. equiv., 256. Found[c]: C, 79.9, 79.9; H, 7.7, 7.7; neut. equiv., 260.

4,5,8-Trimethyl-1,2,3,4-tetrahydro-1-phenanthrone, V.—The acid chloride from 20.0 g. of γ-(5,8-dimethyl-1-naphthyl)-valeric acid and 10 ml. of purified thionyl chloride was dissolved in 200 cc. of anhydrous tetrachloroethane and 11.5 g. of anhydrous aluminum chloride was added in portions to the well-stirred solution maintained below 5°. After standing at room temperature for two hours, the mixture was hydrolyzed with ice-cold 6 *N* hydrochloric acid and the product extracted with benzene. No uncyclized acid was recovered. On distillation under reduced pressure and redistillation, 17.5 g. (94%) of V, b. p. 162–165° at 0.3 mm., was obtained as a pale yellow viscous oil.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found[d]: C, 85.5, 85.8; H, 7.9, 7.9.

The 2,4-dinitrophenylhydrazone melted with decomposition at 285–288° (uncor.).

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[10] All melting points corrected unless otherwise noted. Microanalyses marked [a] by J. A. Curtis, [b] by the Arlington Laboratories, Fairfax, Virginia, [c] by S. R. Olson, [d] by G. Underwood, and [e] by M. M. Ledyard.

[11] Ruzicka and Waldman, *Helv. Chim. Acta*, **15**, 907 (1932); Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

[12] Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

[13] Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

[14] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

[15] Zelinsky and Turowa-Pollack, *Ber.*, **58**, 1295 (1925).

[16] Reference 5, pp. 50–52.

Anal. Calcd. for $C_{23}H_{22}O_4N_4$: N, 13.4. Found[e]: N, 13.5.

1,4,5-Trimethylphenanthrene, VI.—Two grams of V was reduced by the Meerwein–Ponndorf method and the alcohol thus produced was heated at 230–250° for twenty minutes to effect dehydration and was vacuum distilled. The dihydro compound (1.69 g.) was heated at 215–220° with 0.240 g. of sulfur for thirty minutes. After vacuum distillation and crystallization there was obtained 1.03 g. of crude crystalline hydrocarbon, VI, m. p. 55–60°. After careful purification an analytical sample was obtained in the form of colorless plates, m. p. 63.2–63.7°. The 2,4,7-trinitrofluorenone[17] derivative was readily obtained in the form of orange-red small plates, m. p. 184.0–185.8°, after recrystallization from alcohol–benzene. A pure picrate was not obtained as it dissociated so easily on attempted recrystallization.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found[e]: C, 92.8, 92.9; H, 7.2, 7.5. Calcd. for $C_{30}H_{21}O_7N_3$: N, 7.9. Found[e]: N, 8.0.

4,5,8-Trimethyl-3,4-dihydro-1-phenanthrylacetic Acid, VII.—The condensation of 13.5 g. of V with methyl bromoacetate (total of 17 g.) and zinc (total of 90 g.) was carried out and the neutral and dehydrated acidic fractions were isolated essentially as described above for the similar reaction starting with 5,8-dimethyl-1-tetralone. The ethyl ester of VII was obtained as a viscous oil in 74% yield after distillation at 0.3 mm. from a salt heating bath at 215–225°. After several days it set to a crystalline mass, m. p. 42–45°. The acid obtained on hydrolysis formed colorless crystals, m. p. 133.3–135.0°, after several crystallizations from Skellysolve C.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2; neut. equiv. 280. Found[e]: C, 81.5, 81.4; H, 7.2, 7.1; neut. equiv. 280.

4,5,8-Trimethyl-1-phenanthrylacetic Acid.—Dehydrogenation of 2.015 g. of ethyl 4,5,8-trimethyl-3,4-dihydro-1-phenanthrylacetate with 0.2094 g. of sulfur at 230–240° for one-half hour gave 1.80 g. of crude acid after distillation under reduced pressure followed by saponification. Purification by a chromatographic procedure on Norite A using Skellysolve C and acetone gave 0.836 g. (46%) of 4,5,8-trimethyl-1-phenanthrylacetic acid melting above 140°. An analytical sample was obtained as small colorless prisms, m. p. 142.8–143.6°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5; neut. equiv. 278. Found[e]: C, 81.6, 81.9; H, 6.4, 6.4; neut. equiv. 280.

8-Methyl-4,5-dihydro-1-pyrenylacetic Acid.—Further elution of the above column with ether followed by benzene afforded 0.043 g. (2.5%) of an acid melting above 208° with decomposition. If the dehydrogenation was carried out at 240–255°, only 27% VIII but 17% of the higher melting isomer was obtained. An analytical sample melted at 217–218° dec.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.8; neut. equiv., 276. Found[e]: C, 82.5, 82.4; H, 6.0, 6.1; neut. eq., 276.

Resolution of 4,5,8-Trimethyl-1-phenanthrylacetic Acid.—To a warm solution of 1.1026 g. of 4,5,8-trimethyl-1-phenanthrylacetic acid in 40 ml. of absolute ethanol was added a solution of 1.5626 g. of *l*-brucine in 60 ml. of absolute ethyl acetate. The solution was cooled to 15° in a water-bath, seeded with a sample of salt previously obtained, and crystallized with shaking and stirring for fifty minutes. The sample of salt recovered weighed 1.968 g. after drying under vacuum for two hours. A sample of the salt (0.0831 g. in 2.00 ml. of absolute ethyl acetate), gave a rotation of −2.81° in a 2.0 dcm. tube; $(\alpha)^{24}\mathrm{D}$ −33.8°. Two recrystallizations of the salt rapidly from 60 to 70 ml. of 2-1 absolute ethanol–ethyl acetate gave 1.034 g. of material melting at 126.8–128.3° with sintering at 123°.

Anal. Calcd. for $C_{42}H_{44}O_6N_2$: C, 75.0; H, 6.6; N, 4.2. Found[e]: C, 74.4; H, 7.0; N, 4.0.

A sample of the thrice recrystallized salt (0.6128 g. in 20.00 ml. of absolute ethyl acetate) gave a rotation of $-2.01 \pm 0.02°$ in a 2.0 dcm. tube: $(\alpha)^{24.8}\mathrm{D}$ $-32.8 \pm 0.3°$. After 2, 4, 6, 8, 12 and 15 hours at 24.8–24.0°, the rotations observed were −2.06, −2.09, −2.11, −2.13, −2.15, −2.15°, respectively. The specific rotation of the equilibrium mixture was $-35.1 \pm 0.3°$.

4,5,8-Trimethyl-1-phenanthrylacetic acid, VIII, was recovered from 0.4016 g. of thrice recrystallized brucine salt by treatment with 2 ml. of concentrated hydrochloric acid in 15 ml. of water and extracting the liberated acid with ether. The ether solution was then washed with dilute hydrochloric acid, the acid extracted with sodium carbonate and the carbonate extracts acidified. Extraction of the liberated acid with ether, removal of most of the ether under reduced pressure in a stream of dry air and trituration with cold Skellysolve C gave 0.1012 g. of *d*-acid, m. p. 142.4–143.4° (no depression with *dl*-acid).

A solution of 0.0931 g. of *d*-4,5,8-trimethyl-1-phenanthrylacetic acid in 2.00 ml. of chloroform (in a 1.0 dcm. tube), gave an observed rotation of 0.11 ± 0.02; $(\alpha)^{24.8}\mathrm{D}$ $2.3 \pm 0.5°$. After three, four, six and eight hours, the observed rotations were +0.09, +0.06, +0.04 and 0.00°, respectively. In other experiments, samples of *d*-4,5,8-trimethyl-1-phenanthrylacetic acid with rotations of +1.0 to +2.5° were obtained. In some of the first cases, complete racemization had occurred by the time optical measurements were tried.

Summary

The syntheses of 1,4,5-trimethylphenanthrene and 4,5,8-trimethyl-1-phenanthrylacetic acid are described.

Optical activity arising from a new type of steric hindrance between the methyl groups in the four and five positions in the above acid is discussed. It is proposed to call this **optical activity of the 4,5-phenanthrene type.**

COLUMBUS 10, OHIO

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(17) Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946).