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

A New Synthesis and Some Reactions of 4-Phenanthrenecarboxylic Acid

BY KENNETH G. RUTHERFORD[1] AND MELVIN S. NEWMAN

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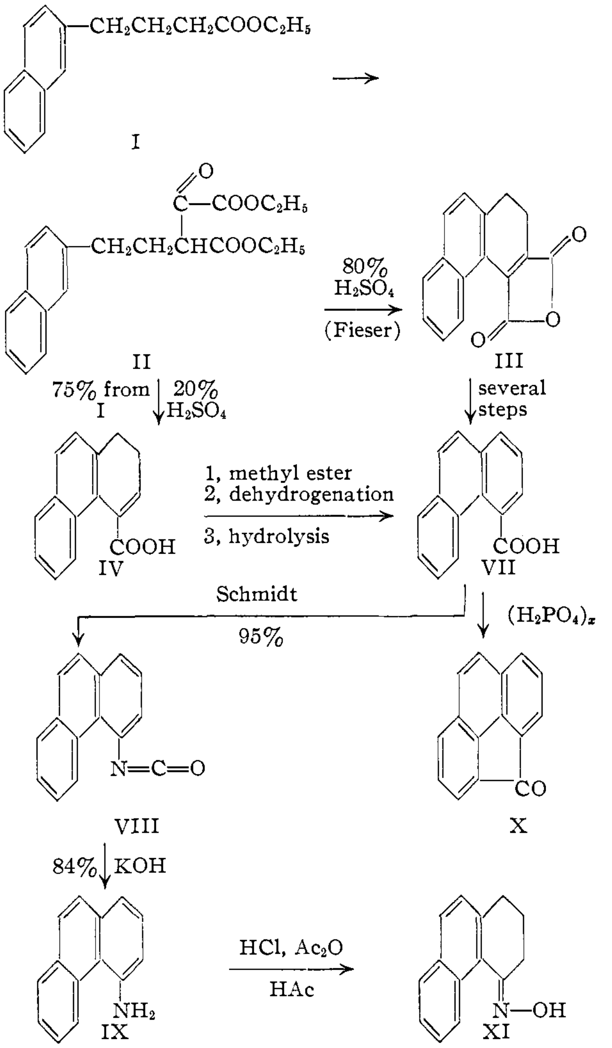
A practical synthesis of 4-phenanthrenecarboxylic acid (VII) and its conversion to 4-aminophenanthrene and 4,5-phenanthrylene ketone is described. The conversion of VII to 4-phenanthrene isocyanate in the Schmidt reaction is also reported.

The first example of a purely aromatic polycyclic hydrocarbon which owes its optical activity to molecular overcrowding was provided by the synthesis and resolution of hexahelicene.[2] In order to extend the program to hepta- and octahelicene,[2b] 4-phenanthraldehyde and 4-bromophenanthrene represent key compounds required if previous synthetic routes are to be applied.[2b,3]

In this paper we report on the preparation of 4-phenanthrenecarboxylic acid (VII) which in principle might provide both of the above compounds. VII has been obtained by fusion of 4,5-phenanthrylene ketone (X) with potassium hydroxide[4] and as one of the oxidation products of 4,5-methylenephenanthrene. VII has also been obtained by several step procedures from ethyl 3-carboethoxy-2-keto-γ-(2-naphthyl)-pentanoate (II) in small over-all yield[5] and α-(1-naphthyl)-glutaric acid.[6]

We have succeeded in cyclizing II in 75% yield to 1,2-dihydro-4-phenanthrenecarboxylic acid (IV) with 20% sulfuric acid (see chart). With dilute acids, II probably undergoes hydrolysis and decarboxylation to the α-ketoacid which then undergoes cyclodehydration to IV. In contrast, with 80% sulfuric acid (Fieser's method[5a]) II first undergoes cyclodehydration which is followed by hydrolysis and further dehydration to give the anhydride III. Conversion of IV to its methyl ester V followed by dehydrogenation afforded methyl 4-phenanthrenecarboxylate (VI) in good yield. On hydrolysis, VI yielded the desired acid VII. With the exception of the dehydrogenation step, which was run in 70-g. lots, the synthesis is adaptable to large scale runs.

When a solution held at 0–5° of VII in a mixture of trifluoroacetic acid and trifluoroacetic anhydride[7] was treated with sodium azide, nitrogen was evolved rapidly and the isocyanate VIII crystallized from solution in 95% yield. It is noteworthy that no mineral acid is required and also that both trifluoroacetic acid and the anhydride were needed as the reaction did not proceed under these conditions when either the acid or the anhydride was used alone. VIII was characterized by elemental analysis, strong absorption at about 4.55μ[8] and by hydrolysis in 84% yield to the known 4-aminophenanthrene (IX). An authentic sample of IX was prepared from the oxime of 4-keto-1,2,3,4-tetrahydrophenanthrene[9] (XI). To our knowledge this is the first isocyanate to be isolated in the Schmidt reaction with organic acids. This fact supports the postulate that a protonated isocyanate is an intermediate in the Schmidt reaction.[10]



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[1] Post-doctoral Fellow, Office of Ordnance Research, contract DA 33-019-ORD-1240, project No. TB 2001(820). This work was supported by a generous grant from the Office of Ordnance Research.

[2] (a) M. S. Newman and D. Lednicer, THIS JOURNAL, **78**, 4765 (1956); (b) helicene is the trivial name for polycyclic aromatic hydrocarbons which have continuously angular ring fusions. The prefix hexa, hepta, etc., refers to the number of rings so fused.

[3] M. S. Newman and R. M. Wise, *ibid.*, **78**, 450 (1956); M. S. Newman and M. Wolf, *ibid.*, **74**, 3225 (1952).

[4] O. Kruber, *Ber.*, **67**, 1000 (1934).

[5] (a) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **57**, 1851 (1935); (b) L. F. Fieser, M. Fieser and E. B. Hershberg, *ibid.*, **58**, 2322 (1936).

[6] M. F. Ansell and D. H. Hey, *J. Chem. Soc.*, 1683, 2874 (1950); F. F. Blicke and R. F. Feldkamp, THIS JOURNAL, **66**, 1087 (1944).

[7] The trifluoroacetic anhydride was prepared by distillation from trifluoroacetic acid and phosphorus pentoxide. With one batch of trifluoroacetic anhydride prepared by a different (unknown to us) method the Schmidt reaction failed.

[8] F. A. Miller in Gilman's "Organic Chemistry," Vol. 3, John Wiley and Sons, Inc, New York, N. Y., 1953, p. 141.

[9] W. Langenbeck and K. Weissenborn, *Ber.*, **72**, 724 (1939).

[10] M. S. Newman and H. L. Gildenhorn, THIS JOURNAL, **70**, 317 (1948).

VII was cyclized in 76% yield with polyphosphoric acid to 4,5-phenanthrylene ketone (X).

Experimental[11]

1,2-Dihydrophenanthrene-4-carboxylic Acid (IV).—Diethyl oxalate (219 g., 1.5 moles) was added to an anhydrous ether (1 liter) slurry of anhydrous powdered potassium ethoxide prepared from 43 g. (1.1 moles) of potassium in absolute ethanol.[12] The solution was cooled to 15° and 242 g. (1 mole) of I dissolved in 300 ml. of anhydrous ether was added under a nitrogen atmosphere. After 24 hours at room temperature the reaction mixture was poured on a mixture of ice and concentrated hydrochloric acid (130 ml.). The ether layer was washed three times with water, dried with sodium sulfate and the ether removed *in vacuo*. The oxalic ester condensation product and excess diethyl oxalate remained as a reddish oil.

After the crude oil was stirred vigorously with 3.5 liters of 20% sulfuric acid at reflux temperature for 96 hours, the aqueous portion was decanted and the remaining semi-crystalline mass dissolved in concentrated potassium carbonate solution. This basic solution was extracted with ether twice and poured slowly with stirring on a mixture of ice and excess hydrochloric acid. The crude acid was filtered and dried. Recrystallization from acetone–Skellysolve F (petroleum ether, b.p. 30–65°) yielded 165 g. (75%) of IV, m.p. 227–233°. A second recrystallization produced colorless needles, m.p. 234.0–234.5°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4; neut. equiv., 224. Found: C, 80.2; H, 5.2; neut. equiv., 227.

Methyl 1,2-Dihydrophenanthrene-4-carboxylate (V).—IV was converted to V in 87% yield by boiling 36 hours with methanolic hydrogen chloride. V crystallized from Skellysolve F in colorless needles, m.p. 70.5–71.5°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.7; H, 5.9.

Methyl 4-Phenanthrenecarboxylate (VI).—V was dehydrogenated by heating with an equivalent of sulfur at 250–260°. The dehydrogenation runs were carried out in 70-g. lots. When hydrogen sulfide evolution slowed measurably (20–30 min.), a small amount of powdered zinc was added and the ester was distilled *in vacuo*. The addition of 50 ml. of cold ethanol to the distillate promoted instantaneous crystallization of VI. The yields ranged from 65–72% of VI, m.p. 78–82°. One recrystallization from methanol yielded colorless plates, m.p. 84.8–85.5°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1. Found: C, 81.3; H, 4.9.

4-Phenanthrenecarboxylic Acid (VII).—Saponification of VI with 10% sodium hydroxide yielded VII quantitatively. Recrystallization of VII from chloroform–Skellysolve F produced colorless plates, m.p. 173.5–174.5°. Melting points of 171.5–173°,[5b] 170–171°[4] and 169–171°[6] have been reported.

4-Phenanthryl Isocyanate (VIII).—VII (5 g., 22.5 mmoles) was dissolved in 100 ml. of a solution which contained equal volumes of trifluoroacetic acid and trifluoroacetic anhydride. The flask was stoppered with a cotton plug, cooled to 0–5° and excess sodium azide was added portionwise with stirring. The reaction proceeded rapidly. Within 5 minutes gas evolution ceased and the isocyanate VIII crystallized. The reaction mixture was allowed to stand at 0–5° with swirling for an additional 5 minutes and then poured on ice. A yield of 4.7 g. (95.5%) of VIII, m.p. 66–68°, was obtained. Recrystallization from Skellysolve F yielded colorless needles, m.p. 68.6–69.0° (strong absorption at 4.55 μ).[9] The reaction did not proceed either in pure trifluoroacetic acid or trifluoroacetic anhydride alone. VIII reacts slowly with moisture and care was needed to obtain the analytical sample.

Anal. Calcd. for $C_{15}H_9ON$: C, 82.1; H, 4.1; N, 6.3. Found: C, 82.0; H, 4.1; N, 6.4.

4-Aminophenanthrene (IX).—A solution of 4.7 g. (21.0 mmoles) of VIII, 3 g. of potassium hydroxide and 130 ml. of 70% ethanol was refluxed for 5 hours. The reaction mixture was poured on ice whereupon IX precipitated. Recrystallization from Skellysolve F afforded 3.5 g. (84%) of IX, m.p. 65–66°. Melting points of 55°[9] and 62.5–63.5°[13] have been reported. IX was prepared independently from the oxime of 4-keto-1,2,3,4-tetrahydrophenanthrene[9] (XI). The melting point coincided with that obtained from the hydrolysis of VIII. The melting point of a mixture was not depressed. The infrared curves were identical.

4,5-Phenanthrylene Ketone (X).—VII (1 g., 4.5 mmoles) was stirred for 60 hours at 100–105° with approximately 30 ml. of polyphosphoric acid.[14] The reaction mixture was then poured on a mixture of ice and potassium carbonate. The precipitate was filtered and dried. Recrystallization from acetone which contained a small amount of chloroform afforded 0.7 g. (76%) of X, m.p. 170.5–171.5° (Kruber[4] reported 170°).

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[11] All melting points are corrected unless otherwise noted. Analyses by Galbraith Laboratories, Knoxville, Tenn.

[12] K. G. Rutherford and C. L. Stevens, THIS JOURNAL, **77**, 3279 (1955).

[13] J. W. Krueger and E. Mosettig, *J. Org. Chem.*, **3**, 345 (1938).

[14] We wish to thank the Victor Chemical Works, Chicago, Ill., for a generous sample of polyphosphoric acid.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE BOTANICAL INSTITUTE, FACULTY OF SCIENCE, UNIVERSITY OF TOKYO]

Anthochlor Pigments of *Coreopsis tinctoria*

BY MASAMI SHIMOKORIYAMA

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From the ray flowers of *Coreopsis tinctoria*, crystals of two anthochlor pigments have been isolated and identified as 4'-glucosidoxy-2',3',3,4-tetrahydroxychalcone (marein) (I) and 6-glucosidoxy-7,3',4'-trihydroxyaurone (maritimein) (V). Marein tends to isomerize into a flavanone glycoside, flavanomarein (III). The latter has also been obtained in crystalline form. Distribution of these three glucosides and other substances in various parts of flowers was studied.

The anthochlor pigments in the composite plants of the sub-tribe *Coreopsidinae*, to which the genera *Coreopsis*, *Cosmos*, *Dahlia*, *Bidens*, etc., belong, have been the subject of many investigations. *Coreopsis tinctoria*, a very commonly cultivated annual or biennial *Coreopsis* in Japan, usually has yellow rays with a red-brown base. A garden variety is often found, in which the red base is spread all over the right surface of the ray flower. The epidermis of the reverse side as well as the mesophyll which lies just under the red part are generally tinged with pale yellow and clearly give a red anthochlor reaction with alkalies. The red part of the upper epidermis contains an anthocyanin which has been identified by Hayashi and Abe[1] as chrysanthemin (cyanidin-3-glucoside).

From the ray flowers two anthochlor glycosides have been isolated which are regarded as major

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[1] K. Hayashi and Y. Abe, Miscellaneous Reports of the Institute for Natural Resources, No. 29, 1 (1953).