IIa and IIb being prepared by Greenstein's procedure.[6] However, this procedure affords IIa more easily than IIb. It is also interesting to note that under identical diazotization conditions, the yield of the resulting α-bromo acids was higher when prepared from alloisoleucine (50%) than isoleucine (35%). This effect may reflect the steric requirements[7] governing the diazotization of amino acids.

A zinc–acetic acid system has been used in many instances to dehalogenate reductively not only α-halo ketones[8] but also α-halo acids. In 1859, Ulrich[9] reduced α-chloropropionic acid to propionic acid with zinc in hydrochloric acid. Paal[10] reported a successful conversion of α-chlorobutyric acid into butyric acid by hydrogenation in the presence of Pd.

$$R{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}COOH \xrightarrow{Zn\ (H_2O)} R{-}CH_2{-}COOH$$

R = CH_3, Bz, *sec*-butyl
X = Cl, Br

Compound *R*-I obtained from IIa ($[\alpha]^{25}D$ +40.0°, 4.5 *N* HCl) exhibited rotation $\alpha^{25}D$ −7.5° (neat, 1 dm). This rotation corresponds to an optical purity of 92%, based on optically pure *S*-I.[11] It is not certain during which step 4% racemization occurred.

When an asymmetric, acyclic, alkylcarboxylic acid does not occur naturally in optically active form, the classical resolution of the asymmetric acid ultilizing alkaloids is often unsuccessful, or, if successful, an extensive purification of the diastereomers by many recrystallizations is usually required.[12] We report the present synthesis as an alternative route for the preparation of optically active, acyclic, alkyl carboxylic acids when the classical alkaloid resolution fails.

Experimental Section

α-Bromo Acids (IIIa and IV).—According to the procedure reported previously,[1] IIIa was prepared in 50% yield from IIa and IV in 35% yield from isoleucine. Nmr spectra showed the α proton as a doublet at 4.20 ppm (J = 6.0 cps) for IIIa and at 4.10 ppm (J = 8.0 cps) for IV.

General Procedure for the Reductive Dehalogenation of α-Halo Acids.—To a dispersion of 15 g (0.25 g-atom) of zinc dust in 500 ml of distilled water was added 0.05 mol of α-halo acid. The resulting mixture was stirred overnight, and, during this time, zinc hydroxide precipitated. When the acid was insoluble in water, the mixture was allowed to reflux for the same time period. The reaction mixture was then acidified with dilute hydrochloric acid and the product acid was extracted with ether. After the ether extract was dried over anhydrous sodium sulfate, distillation afforded dehalogenated acid in almost quantitative yield.

(*R*)-3-Methylpentanoic Acid (*R*-I).—Employing the above procedures, 13 g (0.1 mol) of L-alloisoleucine[6] ($[\alpha]^{25}D$ +40.0°, *c* 1.70 in 4.5 *N* HCl) gave *R*-I {$[\alpha]^{25}D$ −7.5° (neat, 1 dm)} in 50% over-all yield.

(6) J. P. Greenstein, S. M. Birnbaum, and L. Levintow, *Biochem. Prep.*, **3**, 84 (1951).

(7) Assuming that the α-propiolactone intermediate proposed by Neuberger[5] is correct, the attack of nucleophile Br^- would be more hindered in the case of isoleucine.

(8) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 56.

(9) C. Ulrich, *Ann.*, **109**, 268 (1859).

(10) C. Paal and H. Schiedewitz, *Ber.*, **62**, 1935 (1929).

(11) L. Lardicci and L. Conti, *Ann. Chim.* (Rome), **51**, 823 (1961).

(12) For examples, see ref 4; W. von E. Doering and K. B. Wiberg, *J. Amer. Chem. Soc.*, **72**, 2608 (1950); S. Stallberg-Stenhagen, *Ark. Kemi*, **A23**, 14 (1946); J. Cason and R. A. Coad, *J. Amer. Chem. Soc.*, **72**, 4695 (1950).

Registry No.—*R*-I, 16958-25-1.

Acknowledgment.—The financial support of Research Laboratory, U. S. Army, Edgewood Arsenal, is gratefully acknowledged.

A New Synthesis of 11H-Indeno[2,1-*a*]phenanthrenes

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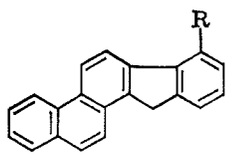
The incentive for the synthesis of 11H-indeno[2,1-*a*]phenanthrene (**1**) and its alkyl derivatives stems from a desire to prepare materials of known structure for comparison with certain complex dehydrogenation products. Steroids in particular furnish an array of dehydrogenation products,[2] among which indenophenanthrenes have been recognized.[3-8] The structures of several of these pentacyclic dehydrogenation products are unknown;[2] the compounds presumably arise from unknown or unrecognized transformations.



1, R = H
2, R = CH_3

All previous syntheses[7-12] of substituted 11H-indeno[2,1-*a*]phenanthrenes have a common characteristic. A partially aliphatic precursor with the same skeletal features as the desired compound is first synthesized, and then this precursor is aromatized by dehydrogenation. Since the syntheses produce the comparison samples by dehydrogenation methods which may promote obscure transformations, the conclusions based on comparisons with these samples lack logical rigor. While the results and conclusions of earlier workers may not eventually prove to be invalid, they certainly warrant reinvestigation.

Obviously, a synthesis of 11H-indeno[2,1-*a*]phenanthrenes which does not include dehydrogenation would be highly desirable. This objective has been

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(2) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1949, pp 147–156.

(3) W. O. Godtfredsen and S. Vangedal, *Tetrahedron*, **18**, 1029 (1962).

(4) H. Dannenberg and H.-G. Neumann, *Ann.*, **646**, 148 (1961); *Ber.*, **94**, 3085 (1961).

(5) D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 5275 (1956).

(6) W. R. Nes and E. Mosettig, *ibid.*, **76**, 3182 (1954).

(7) J. W. Cook, C. L. Hewett, W. V. Mayneord, and E. Roe, *J. Chem. Soc.*, 1727 (1934).

(8) W. E. Bachmann, J. W. Cook, C. L. Hewett, and J. Iball, *ibid.*, 54 (1936).

(9) D. Nasipuri and D. N. Roy, *ibid.*, 3361 (1961).

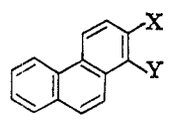
(10) E. Buchta and H. Krätzer, *Ber.*, **95**, 1820 (1962).

(11) B. B. Datta and J C. Bardhan, *J. Chem. Soc.*, 3974 (1962).

(12) S. Uyeo, T. Mizutani, A. Yoshitake, and A. Ito, *Yakugaku Zasshi*, **84**, 458 (1964); *Chem. Abstr.*, **61**, 4286 (1964).

achieved. A method[13] which proved to be successful in the synthesis of chrysofluorene derivatives has been modified and extended, and it serves as a synthesis of the pentacyclic ring system.

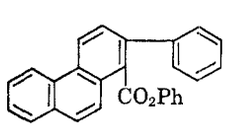
The key intermediate in this synthesis is phenyl 2-methoxy-1-phenanthrenecarboxylate (**3**). In a fashion that parallels the behavior of the hindered phenoxycarbonyl group of phenyl 2-methoxy-1-naphthoate,[13] the ester group of **3** is not extensively attacked by an aromatic Grignard reagent, even when the reagent is present in large excess. Rather, the organic portion of the Grignard reagent replaces the methoxyl group instead. Hence, this treatment joins two fully aromatic fragments at specific points, and no aromatization step is required. Moreover, an aryl group thus joined to the phenanthrene nucleus undergoes cyclization with the surviving ester group, which affords a second unambiguous point of attachment to the tricyclic nucleus.



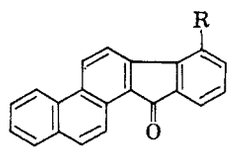
3, X = OCH_3; Y = CO_2Ph
4, X = OH; Y = H
5, X = OCH_3; Y = H
6, X = OCH_3; Y = CHO
7, X = OCH_3; Y = CO_2H

The key intermediate was prepared by the following sequence of reactions. Barium 2-phenanthrenesulfonate was isolated from the sulfonation products of phenanthrene.[14] Alkali fusion of the barium salt gave 2-phenanthrol (**4**)[15] which was methylated by the procedure of Mosettig and Stuart.[16] Formylation of the 2-methoxyphenanthrene (**5**) with dimethylformamide and phosphorus oxychloride gave 2-methoxy-1-phenanthrenecarboxaldehyde (**6**) in good yield. Permanganate oxidation of the aldehyde furnished the corresponding acid (**7**) which was converted into the phenyl ester (**3**) *via* the acid chloride.

The unusual and distinctive step in the synthesis is the reaction between the key intermediate and a Grignard reagent. Treatment of **3** with phenylmagnesium bromide furnishes phenyl 2-phenyl-1-phenanthrenecarboxylate (**8**) in 80% yield.



8



9, R = H
10, R = CH_3

The phenyl ester **8** can be used directly in a ring-closure step with sulfuric acid. When **8** is allowed to stand in the concentrated acid for a short time, 11H-indeno[2,1-*a*]phenanthren-11-one (**9**) is produced in 71% yield. Finally, the sequence was completed by the modified Wolff–Kishner reduction devised by Weisburger and Grantham[17] which served admirably to produce pure 11H-indeno[2,1-*a*]phenanthrene (**1**) in excellent yield from **9**.

Products of the methoxyl group replacement, such as **8**, are isolated and purified with difficulty; however, use of crude material in the ring closure was not detrimental to the purity of the ketone **9** which was isolated in an over-all yield of 61% for the combined operations of replacement and ring closure.

Attention was next directed toward the preparation of an alkylated derivative. For comparison purposes, the 7-methyl derivative was chosen as the objective, because it alone of the alkylated derivatives had been prepared by several independent methods.[8-10] The combined operations of replacement of the methoxyl group by the organic portion of *o*-tolylmagnesium bromide and the ring closure effected by sulfuric acid gave 7-methyl-11H-indeno[2,1-*a*]phenanthren-11-one (**10**) in 49% yield. The modified Wolff–Kishner reduction afforded 7-methyl-11H-indeno[2,1-*a*]phenanthrene (**2**) in high yield.

An important observation deserves comment. The melting points of the polycyclic ketones **9** and **10** are appreciably influenced by traces of acid. Care must be exercised in ensuring removal of residual traces of acid remaining from previous steps in its preparation and in the avoidance of acidic crystallization media. When these precautions are observed, a more brightly colored product of higher melting point results.

Experimental Section

Melting points were determined in capillaries inserted into a heated aluminum block provided with a thermometer calibrated to 300°. Analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California.

Barium 2-Phenanthrenesulfonate.—This salt was isolated in pure form in 20% yield from the sulfonation products of phenanthrene.[14]

2-Phenanthrol (**4**).—Alkali fusion of barium 2-phenanthrenesulfonate yielded 2-phenanthrol, mp 166.5–167.5° (lit.[15] mp 168°) in 78% yield.

2-Methoxyphenanthrene (**5**).—Methylation of 2-phenanthrol by the procedure of Mosettig and Stuart[16] gave 2-methoxyphenanthrene, mp 98.5–99° (lit.[18] mp 100–101°), in 98% yield.

2-Methoxy-1-phenanthrenecarboxaldehyde (**6**).—A mixture of 10.4 g of 2-methoxyphenanthrene, 8.5 ml of dimethylformamide, and 10.5 ml of phosphorus oxychloride was heated for 6 hr on the steam bath and poured into a mixture of ice and 200 ml of saturated sodium acetate solution. The precipitate was collected, washed with copious amounts of water, dried in air, and crystallized from chlorofor–methanol to give 8.2 g (69%) of 2-methoxy-1-phenanthrenecarboxaldehyde (**6**) as bright yellow needles, mp 159.5–161.5°. A small sample after recrystallization from the same solvent pair exhibited mp 161–161.5°; this aldehyde had previously been obtained as light brown crystals, mp 160°.[19]

2-Methoxy-1-phenanthrenecarboxylic Acid (**7**).—To a suspension of 7.09 g of the aldehyde **6** in 150 ml of boiling acetone, 9.5 g of potassium permanganate in 200 ml of warm water was added with stirring over a period of 40 min. Stirring was continued for 1.5 hr while the temperature was maintained between 75 and 80°. A solution of 4 g of potassium hydroxide in 40 ml of water was added and the reaction mixture was filtered while warm. The filtrate and two washes of the precipitated manganese dioxide were cooled to 0° and acidified with hydrochloric acid. The yellowish precipitate was crystallized from ethanol–water to afford 4.98 g (66%) of the colorless methoxy acid, mp 247–248.5°, with gas evolution (lit.[19] mp 244–246° dec).

Phenyl 2-Methoxy-1-phenanthrenecarboxylate (**3**).—A mixture of 4.94 g of 2-methoxy-1-phenanthrenecarboxylic acid and 15 ml

(13) R. C. Fuson and F. W. Wassmundt, *J. Amer. Chem. Soc.*, **78**, 5409 (1956).
(14) L. F. Fieser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 482.
(15) L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 2460 (1929).
(16) E. Mosettig and A. H. Stuart, *ibid.*, **61**, 1 (1939).
(17) J. H. Weisburger and P. H. Grantham, *J. Org. Chem.*, **21**, 1160 (1956).
(18) A. Werner and K. Rekner, *Ann.*, **321**, 305 (1902).
(19) E. Mosettig and A. Burger, *J. Amer. Chem. Soc.*, **55**, 2981 (1933).

of thionyl chloride was allowed to stand overnight and was then heated under reflux 1.5 hr before removal of the excess thionyl chloride under reduced pressure. To the residue was added 2.00 g of phenol in 25 ml of benzene, and the resulting mixture was boiled under reflux for 1 hr. Filtration and cooling of the solution after clarification with charcoal yielded 5.73 g (89%) of the phenyl ester, mp 147.5–149°. A crystallization from acetone–water gave needles, mp 150–150.5°.

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.66; H, 4.79.

Phenyl 2-Phenyl-1-phenanthrenecarboxylate (8).—A suspension of 1.00 g of phenyl 2-methoxy-1-phenanthrenecarboxylate in 20 ml of benzene was added to the Grignard reagent prepared from 0.24 g of magnesium and 1.88 g of bromobenzene in 15 ml of ether. The reaction mixture was heated under reflux for 2.5 hr and hydrolyzed with ice and ammonium chloride. The organic layer and three benzene extracts of the aqueous portion were combined. Steam distillation removed the organic solvents and a small amount of biphenyl. The residue from the distillation was separated by filtration and dried in air. Crystallization from acetone afforded 0.91 g (80%) of white crystals, mp 185–186°. Sublimation in high vacuum gave an analytically pure sample mp 185.5–186°.

Anal. Calcd for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.28; H, 4.75.

11H-Indeno[2,1-*a*]phenanthren-11-one (9). From Pure 8.—A solution of 100 mg of the ester **8** in 5 ml of concentrated sulfuric acid was allowed to stand at room temperature for 1.5 hr. The permanganate-colored mixture was poured into ice water, and the resulting yellow precipitate was collected by filtration, washed with 5% aqueous sodium carbonate and water, and dried in air to give 53 mg (71%) of material, mp 207–212°. Crystallization from ethyl acetate gave golden yellow needles of the ketone **9**, mp 213.5–214°; crystallization from acetic acid produced a darker product melting over a wider range at a lower temperature. The sample crystallized from acetic acid had properties more in keeping with those described in the literature[7] (reddish orange needles, mp 207–208°).

11H-Indeno[2,1-*a*]phenanthren-11-one (9). From 3 without Isolation of Pure 8.—A solution of 657 mg of phenyl 2-methoxy-1-phenanthrenecarboxylate (**3**) in 40 ml of benzene was added to the Grignard reagent prepared from 0.24 g of magnesium and 1.88 ml of bromobenzene in 15 ml of ether. The reaction mixture was heated under reflux for 2.5 hr and hydrolyzed with ice and ammonium chloride. The organic layer and three benzene extracts of the aqueous portion were combined and steam distilled. The solid in the cooled residue was separated by filtration and dried in air. The solid was next stirred into 15 ml of concentrated sulfuric acid and allowed to stand at room temperature for 1.5 hr. The permanganate-colored mixture was poured onto ice; the resulting precipitate was collected by filtration and washed with 5% aqueous sodium carbonate solution and water. Crystallization of the dried material from ethyl acetate furnished 341 mg (61%) of **9** as golden yellow needles, mp 214–214.5°.

11H-Indeno[2,1-*a*]phenanthrene (1).—The ketone **9** was reduced by the Wolff–Kishner reaction as modified by Weisburger and Grantham.[17] A suspension of 36 mg of ketone **9** in 20 ml of distilled diethylene glycol and 2 ml of 85% hydrazine hydrate was warmed at 100° for 5 min; 1 ml of 10% potassium hydroxide in the same solvent was added; and the solution was kept at 100° for 10 min longer. Water was driven off until the temperature rose to 200°; further heating for 2 hr was continued under reflux. The reaction mixture was cooled and poured into 100 ml of cold water and filtered. The solids were washed with water and dried in air to give 27.4 mg (80%) of the crude hydrocarbon, mp 330–331° (uncor). Crystallization from benzene gave blades, mp 331–332° (uncor) and 335–336° (uncor, in a sealed, evacuated capillary) (lit.[11] mp 335–336°).

7-Methyl-11H-indeno[2,1-*a*]phenanthren-11-one (10).—A solution of 200 mg of **3** in 6 ml of benzene was added to the Grignard reagent prepared from 82 mg of magnesium and 0.48 ml of *o*-bromotoluene in 8 ml of ether. Treatment of the reaction mixture was similar to that described for the direct preparation of **9** from **3**. Crystallization of the crude, dry ketone from ethyl acetate gave 89 mg (49%) of **10** as yellow needles, mp 211–212°. After sublimation and recrystallization from ethyl acetate, the ketone melted at 213–214° (lit.[8] mp 209–210°).

7-Methyl-11H-indeno[2,1-*a*]phenanthrene (2).—Reduction of 20 mg of the ketone **10** by the procedure described for the preparation of **1** gave 16 mg (84%) of the crude, colorless hydrocarbon, mp 272.5–274°. Sublimation followed by crystallization from ethyl acetate gave colorless crystals, mp 274–275° (lit.[8] mp 275–276°).

Registry No.—**1**, 220-97-3; **2**, 16793-26-3; **3**, 16793-27-4; **8**, 16793-28-5; **9**, 4599-92-2; **10**, 16793-30-9.

10-Hydroxy-10,9-boroxarophenanthrene. A Lewis Acid[1]

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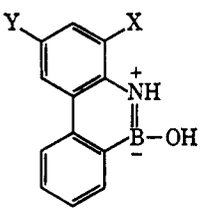
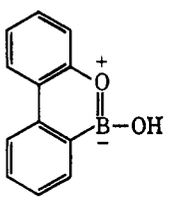
Received April 9, 1968

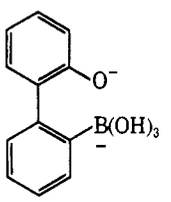
A large number of boron-containing heteroaromatic compounds, isoelectronic with "normal" aromatic systems and derived from them by replacing a pair of adjacent carbon atoms by boron and nitrogen or boron and oxygen, are now known.[3] At an early stage, it was shown that the ultraviolet spectra of 10-hydroxy-10,9-borazarophenanthrene (Ia),[4] and of 10-hydroxy-10,9-boroxarophenanthrene (II)[5] in neutral and alkaline so-



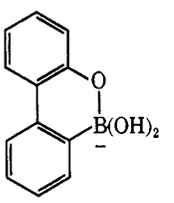
Ia, X = Y = H
b, X = H; Y = NO_2
c, X = NO_2; Y = H



II



III



IV

lution suggested that these compounds behaved as protic acids, unlike normal boronic or borinic acids that seem to form salts by addition to boron. This difference was attributed to aromatic stabilization of the boron-containing rings, and indeed was cited as evidence that such compounds are aromatic. Since that time it has usually been assumed that other analogous hydroxyborazaro and hydroxyboroxaro compounds show similar behavior to base by acting as protic acids, rather than Lewis acids.

Recently[6] it was shown that ^{11}B nmr spectroscopy provides a simple and unambiguous criterion of the mode of

(1) This work was supported by a grant from The Robert A. Welch Foundation.

(2) Robert A. Welch Postdoctoral Fellow, 1966–1968.

(3) See M. J. S. Dewar, *Prog. Boron Chem.*, **1**, 235 (1964); R. F. Gould, "Boron-Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 227.

(4) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

(5) M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 1344 (1960).

(6) M. J. S. Dewar and R. Jones, *J. Amer. Chem. Soc.*, **89**, 2408 (1967).