Reaction of Some Substituted Phenanthrenes with n-Butyllithium

BY HENRY GILMAN AND THOMAS H. COOK

In extension of interconversion reactions of organolithium compounds, an examination has been made of the halogen–metal and hydrogen–metal interconversion reactions of some substituted phenanthrenes.

Halogen–Metal Interconversion Reactions.—The following halogen–metal interconversion reaction has been effected with 2-, 3-, and 9-bromophenanthrenes and n-butyllithium.

$$C_{14}H_9Br + n\text{-}C_4H_9Li \longrightarrow C_{14}H_9Li + n\text{-}C_4H_9Br \quad [A]$$
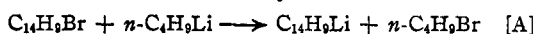
Carbonation by solid carbon dioxide gave the corresponding 2-, 3-, and 9-phenanthrenecarboxylic acids.

Müller and Töpel[1] observed that 9-bromophenanthrene reacted slowly with lithium in ether, and that after deposition of a colorless precipitate an intense dark blue color set in on shaking. They suggested that the organolithium compound which had formed decomposed the ether promptly, and that the resulting phenanthrene then added two atoms of lithium in the 9,10-positions in the usual manner.[2] There is no evidence in our studies to support their idea that 9-phenanthryllithium promptly decomposes ether. These authors also state that α-naphthyllithium decomposes ether "very quickly." This, too, is contrary to our experience, for not only is α-naphthyllithium obtainable in 96% yield by direct reaction of α-bromonaphthalene and lithium in ether,[3a] but in a halogen–metal interconversion reaction like [A] α-naphthyllithium is obtainable in a 97% yield (on the basis of α-naphthoic acid prepared from it by carbonation) from α-bromonaphthalene and n-propyllithium in ether.[3b] The general evidence points to the probable formation of aryllithium compounds in 90% or better yields by the interconversion reaction.[3c] The only known RLi compounds which decompose ether promptly are the s-butyl- and t-butyllithiums.[3d]

Metalation of Hydroxy- and Methoxyphenanthrenes.—In the metalation of phenols and their

ethers by n-butyllithium, the hydrogen in an ortho position is replaced by lithium; and, in general, the yield of metalation products is greater with the ethers than with the phenols. Where isomeric mono-metalation products are possible, as with 2-hydroxydibenzofuran and resorcinol (or their methyl ethers), sometimes the phenols and sometimes the ethers give but one monometalation product.[4]

2-Methoxyphenanthrene is metalated by n-butyllithium to give 2-methoxy-3-phenanthryllithium; and 3-methoxyphenanthrene is metalated to give 3-methoxy-2-phenanthryllithium. The structures of these compounds were established by carbonating or oxidizing the RLi compounds to their respective methoxy-acids and methoxyphenols. A schematic representation of the several transformations is given below.

The identity of compounds I, V, VI and VII was completed by comparison with specimens kindly provided by Dr. Erich Mosettig. A particularly significant series of transformations establishing the orientation is that culminating in the formation of 2,3-dimethoxyphenanthrene [V], inasmuch as both the 2-methoxyphenanthrene and the 3-methoxyphenanthrene give the same dimethoxyphenanthrene.

2-Hydroxyphenanthrene was metalated to a very small extent, and carbonation gave 2-hydroxy-3-phenanthrenecarboxylic acid. This product was methylated to a methoxy-acid shown to be identical with the 2-methoxy-3-phenanthrenecarboxylic acid [I] obtained from 2-methoxyphenanthrene and metalation followed by carbonation. In an attempted metalation of 3-hydroxyphenanthrene most of the phenol was recovered, as was the case in the successful metalation of 2-hydroxyphenanthrene. The small quantity of resin resulting from this reaction may have been associated with a less stable ortho-hydroxy acid, for it was precipitated by acid from a bicarbonate solution.

9-Hydroxyphenanthrene and 9-methoxyphenanthrene gave particularly interesting products. Metalation of 9-methoxyphenanthrene followed

(1) Müller and Töpel, *Ber.*, **72**, 281 (1939).

(2) See Jeanes and Adams, THIS JOURNAL, **59**, 2608 (1937), for the addition of alkali metals to phenanthrene, together with references to the earlier literature.

(3) (a) Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933). (b) Gilman and Moore, *ibid.*, **62**, 1843 (1940). (c) See earlier studies in this series, particularly with bromodibenzofurans. (d) Studies by F. W. Moore and O. Baine.

(4) Gilman, Willis, Cook, Webb and Meals, THIS JOURNAL, **62**, 667 (1940).
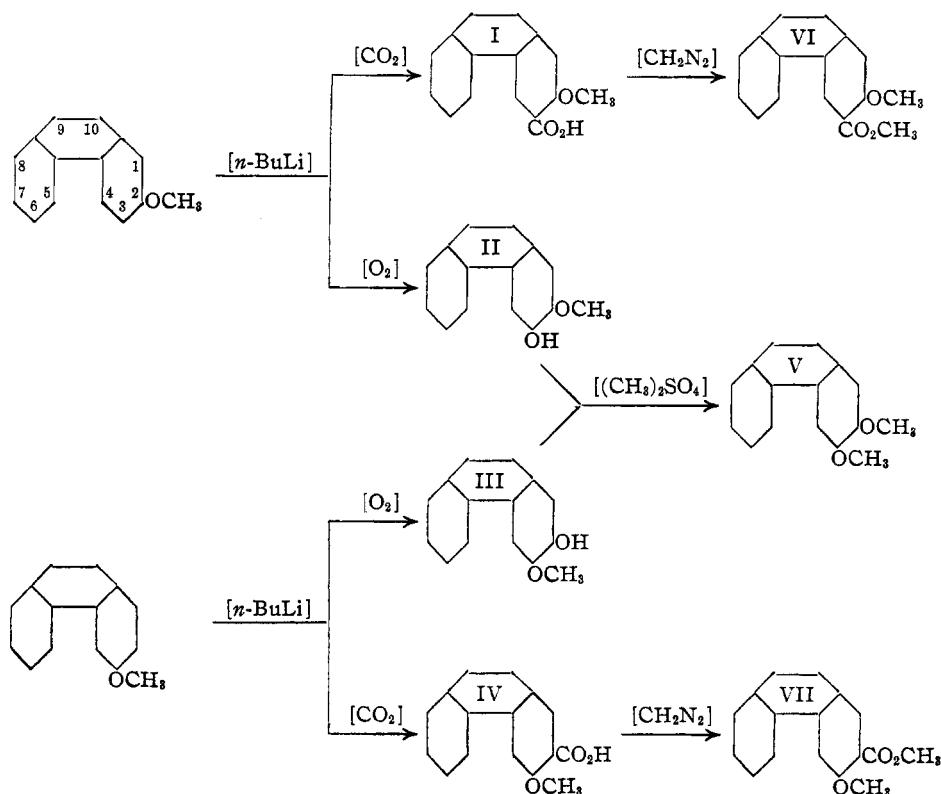
by carbonation gave two products. One of these was shown by comparison with an authentic specimen to be 9-methoxy-10-phenanthrenecarboxylic acid. The other product, 9 - methoxy - x - phenanthrenecarboxylic acid, was identical with the product obtained from 9-hydroxyphenanthrene by metalation, followed successively by carbonation and methylation.

because of the availability of the 10- or ortho-position was not isolated.[5]

3-Hydroxy-2-phenanthrenecarboxylic Acid.— Werner and Kuntz[6] carried out a Kolbe reaction on 3-hydroxyphenanthrene and assigned to the product the structure of 3-hydroxy-2-phenanthrenecarboxylic acid, although the alternative ortho isomer (3-hydroxy-4-phenanthrenecarbox-
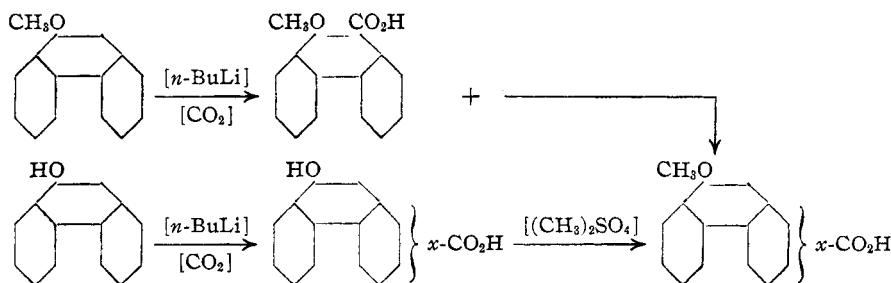
The x-acids obtained from both the 9-hydroxy- and 9-methoxyphenanthrenes are of especial importance because they appear to be the first known cases where metalation does not take place ortho to a phenol or methoxy group. It is of even greater significance with 9-hydroxyphenanthrene for the acid, 9-hydroxy-10-phenanthrenecarboxylic acid, that certainly would have been expected

ylic acid) had some plausibility. Mosettig and Burger[7] repeated their work; then excluded 3-hydroxy-4-phenanthrenecarboxylic acid as a pos-

(5) The low yields of metalation products of phenols may have been responsible for the non-isolation of any 9-hydroxy-10-acid. The study is being continued, and an orienting experiment attempted to throw some light on the structure of the x-acids is described in the Experimental Part.

(6) Werner and Kuntz, Ber., 35, 4424 (1902).

(7) Mosettig and Burger, THIS JOURNAL, 55, 2981 (1933).

sibility by synthesizing the corresponding methoxy acid from the 3-methoxy-4-phenanthrenealdehyde of Smith[8]; and concluded on firmer grounds that the Kolbe product was 3-hydroxy-2-phenanthrenecarboxylic acid. Because of some anomalous reactions of phenanthrene derivatives (particularly those involving some Fries rearrangements and Friedel–Crafts reactions, and perhaps the Kolbe reaction), our proof of the structure of 3-hydroxy-2-phenanthrenecarboxylic acid and the establishment of its identity with the Kolbe product, are convincing evidence for the correctness of the structure assigned by Werner and Kuntz and by Mosettig and Burger.

Dimorphism.—We have observed dimorphic forms of methyl 2-methoxy-3-phenanthrenecarboxylate. Recent illustrations of polymorphism in the phenanthrene series have been reported by Bachmann.[9]

Metalation of Phenanthrene.—In a recent general study on metalation,[10] it was reported that the metalation of phenanthrene yielded only small amounts of 9-fluorenecarboxylic acid. This supported the observation of others[2] that fluorene is a contaminant in some specimens of phenanthrene. Incidental to a study on the metalation of polynuclear compounds, Mr. R. W. Leeper has observed that phenanthrene can be metalated in the 9-position by alkyllithium compounds, and that the controlled reaction may be serviceable as a stage in the purification of technical phenanthrene.

Experimental Part

Reactions of n-Butyllithium with the 2- and 3- and 9-Bromophenanthrenes.—The 2- and 3-bromophenanthrenes were prepared by the following sequence of reactions: phenanthrene ⟶ acetylphenanthrene ⟶ oxime ⟶ acetamide ⟶ amine ⟶ bromophenanthrene.[11] 9-Bromophenanthrene was prepared by decomposing the pure 9,10-dibromo-9,10-dihydrophenanthrene of Price and co-workers[12] as described by Austin,[13] and distilling the product under reduced pressure.[14]

A mixture of 1 g. (0.0039 mole) of 2-bromophenanthrene in 25 cc. of ether and 0.006 mole of n-butyllithium[15] in ether was refluxed in a nitrogen atmosphere for one-half hour and then carbonated by pouring upon crushed solid

carbon dioxide. The ether was distilled from the carbonation mixture, and the residue was then extracted with hot 5% sodium hydroxide solution. After treatment with Norit the alkaline solution was filtered and acidified. The yield of 2-phenanthrenecarboxylic acid melting at 258–260° was 0.32 g. or 37%. Identification was completed by a mixed melting point determination with an authentic specimen of the acid prepared from 2-acetylphenanthrene,[11b] and also by converting the acid to methyl 2-phenanthrenecarboxylate which likewise was compared with an authentic specimen (mixed melting point, 93–95°).

From 2 g. (0.0078 mole) of 3-bromophenanthrene and 0.012 mole of n-butyllithium in 100 cc. of ether, under the conditions described for the 2-bromophenanthrene, was isolated 0.55 g. or 32% of 3-phenanthrenecarboxylic acid melting at 270–272°. Identification was again completed by mixed melting points with the acid[11b] and of the corresponding methyl ester (m. p. 93–94°).

A solution of 2.25 g. (0.0088 mole) of 9-bromophenanthrene and 0.01 mole of n-butyllithium was refluxed for four hours, carbonated, and then worked up in the manner described for the 2-bromophenanthrene. The yield of 9-phenanthrenecarboxylic acid melting at 254–256° was one gram or 51%. The acid was converted by the action of diazomethane to methyl 9-phenanthrenecarboxylate (m. p. 114–115°), and this ester showed no depression in a mixed melting point determination with the ester prepared from a specimen of the acid obtained by carbonating the Grignard reagent of 9-bromophenanthrene.[14]

The three halogen–metal interconversion reactions were carried out before optimal conditions were devised for such reactions, and it is highly probable that the yields can be significantly improved by a few simple alterations in procedure using the convenient technique of removing aliquots.[3b]

Metalation of 2 - Hydroxyphenanthrene.—The 2-hydroxyphenanthrene was prepared by the alkaline fusion of barium 2-phenanthrenesulfonate,[16] and also from 2-phenanthrylamine by the diazo reaction.[11] A solution of 2 g. (0.01 mole) of 2-hydroxyphenanthrene and 0.03 mole of n-butyllithium in 60 cc. of a 1:1 mixture of ether–benzene was refluxed and stirred for fifteen hours. In addition to an 82.5% recovery of 2-hydroxyphenanthrene there was obtained, subsequent to carbonation, 30 mg. or 1.5% of 2-hydroxy-3-phenanthrenecarboxylic acid melting at 276–277° (with prior sintering).

Anal. Calcd. for $C_{15}H_{10}O_3$: neut. equiv., 238. Found: neut. equiv., 230.

Twenty-five milligrams of the 2-hydroxy-3-phenanthrenecarboxylic acid was converted in a 40% yield by the action of methyl sulfate and potassium hydroxide, to 2-methoxy-3-phenanthrenecarboxylic acid (I). There was no depression in a mixed melting point determination (211–213°) of the methoxy-acid with the acid obtained from 2-methoxyphenanthrene by metalation and carbonation.

Metalation of 2-Methoxyphenanthrene. [A] Carbonation.—The 2-hydroxyphenanthrene was methylated by a modification of the procedure used by Stevens and Tucker[17] with carbazole. A solution of (0.005 mole) of 2-methoxy-

(8) Smith, *J. Chem. Soc.*, **109**, 568 (1916); Barger, *ibid.*, **113**, 218 (1918).

(9) Bachmann, THIS JOURNAL, **57**, 555 (1935).

(10) Gilman and Bebb, *ibid.*, **61**, 109 (1939).

(11) (a) Bachmann and Boatner, *ibid.*, **58**, 2194 (1936);   (b) Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

(12) Price, Arntzen and Weaver, *ibid.*, **60**, 2837 (1938).

(13) Austin, *J. Chem. Soc.*, **93**, 1763 (1908).

(14) Bachmann, THIS JOURNAL, **56**, 1365 (1934).

(15) Gilman, Zoellner, and Selby, *ibid.*, **54**, 1957 (1932); Gilman Langham and Moore, *ibid.*, **62**, 2327 (1940).

(16) Fieser, *ibid.*, **51**, 2460 (1929); "Organic Syntheses," **16**, 63 (1936).

(17) Stevens and Tucker, *J. Chem. Soc.*, **123**, 2140 (1923).

phenanthrene and 0.01 mole of *n*-butyllithium in 40 cc. of ether was stirred and refluxed for fifteen hours and then carbonated to give 0.67 g. or 55% of crude acid. After recrystallization from water (as the potassium salt) and then from ethanol, the yield of 2-methoxy-3-phenanthrene-carboxylic acid (I) melting at 211–213° was 0.47 g. or 39%. Identification was completed by a mixed melting point determination with a sample prepared by Mosettig and Stuart.[18,19]

Anal. Calcd. for $C_{16}H_{12}O_3$: neut. equiv., 252. Found: neut. equiv., 249.

The ether solution from the metalation reaction yielded 0.45 g. or a 45% recovery of 2-methoxyphenanthrene.

Methylation of our 2-methoxy-3-phenanthrenecarboxylic acid by diazomethane gave an ester (VI) which melted at 77–78° and not at 94–95° as reported earlier.[18] However, after standing as a dry solid for one week, the 77–78° ester had changed to give a melting point range of 77–94°. This material, after crystallizing from dilute methanol, and then seeding with a crystal of the ester prepared by Mosettig and Stuart,[18] melted at 94–95°, and showed no depression in a mixed melting point determination with the 94–95° specimen.[18,19].

[B] **Oxidation.**—A solution of 10.4 g. (0.05 mole) of 2-methoxyphenanthrene and 0.55 mole of *n*-butyllithium in 100 cc. of ether was refluxed for nineteen hours, cooled in an ice-bath, and then, after adding 0.055 mole of *n*-butyl-magnesium bromide,[20] oxidized by admitting a stream of air (free of carbon dioxide) until a negative color test for RM compounds was obtained.[21] During the oxidation, a precipitate formed and the mixture became light gray in color. The yield of 2-methoxy-3-hydroxyphenanthrene (II) melting at 145–146° after two crystallizations from 50% ethanol and one crystallization from petroleum ether (b. p. 60–68°) was 2 g. or 18.5%.

Anal. Calcd. for $C_{15}H_{12}O_2$: OCH_3, 13.83. Found: OCH_3, 13.97.

From the alkaline extract of the ether–water mixture (which was filtered from the original oxidation precipitate of 4.7 g. melting between 122–143°) was obtained 1.3 g. of a low melting product which has not as yet been resolved. It appears probable that isomers were formed in the metalation.

To 0.5 g. of 2-methoxy-3-hydroxyphenanthrene in 10 cc. of acetone and 3 cc. of 50% potassium hydroxide was added 1 g. of methyl sulfate. The mixture was heated on a water-bath for one hour, and then yielded (by customary procedures) 0.29 g. or 54.5% of 2,3-dimethoxyphenanthrene (V) melting at 132.5–133.5° after crystallization from ethanol. The melting point of this compound was not depressed when admixed with authentic 2,3-dimethoxyphenan-threne[19,22] or with the dimethoxy compound obtained from 3-methoxyphenanthrene by metalation, oxidation, and methylation. This latter procedure appears to be more satisfactory for the preparation of 2,3-dimethoxyphenan-

threne, both from the standpoint of yield and number of steps involved, than the earlier methods, which have involved ring closure syntheses.

Apparently 3-hydroxyphenanthrene is less readily metalated than the 2-isomer. In an orienting experiment, a mixture of 2 g. (0.01 mole) of 3-hydroxyphenanthrene and 0.03 mole of *n*-butyllithium in a 1:1 ether–benzene solution was refluxed and stirred for sixteen hours prior to carbonation. The recovery of 3-hydroxyphenanthrene was 1.6 g. or 80%, in addition to 50 mg. of a resin obtained by acidification of the bicarbonate solution. It should be noted that although in this metalation experiment the medium again used was an ether–benzene mixture, it is now known that metalations proceed more slowly in benzene than in ether, and more effectively in di-*n*-butyl ether than in diethyl ether.[10]

2-Methoxy-3-acetoxyphenanthrene.—To a suspension of 0.5 g. of 2-methoxy-3-hydroxyphenanthrene in 10 cc. of acetic anhydride was added one drop of concd. sulfuric acid, and after three minutes the mixture was poured into water. The yield of 2-methoxy-3-acetoxyphenanthrene melting at 146–147° after crystallization from ethanol was 0.3 g. or 50%.

Anal. Calcd. for $C_{17}H_{14}O_3$: OCH_3, 11.66. Found: OCH_3, 11.81.

Metalation of 3-Methoxyphenanthrene. [A] Carbonation.—A solution of 0.75 g. (0.0036 mole) of 3-methoxy-phenanthrene in 20 cc. of ether was refluxed for fifteen hours with 1.5 equivalents of *n*-butyllithium. Subsequent to carbonation, there was isolated 0.3 g. or 33% of 3-methoxy-2-phenanthrenecarboxylic acid (IV) melting at 185° after crystallization from glacial acetic acid.

Anal. Calcd. for $C_{16}H_{12}O_3$: neut. equiv., 252. Found: neut. equiv., 247.

Methyl 3-methoxy-2-phenanthrenecarboxylate (VII) (prepared from the methoxy-acid by diazomethane, and melting at 134–134.5°) was shown to be identical with an authentic specimen.[19]

[B] **Oxidation.**—A solution of 0.72 g. (0.0035 mole) of 3-methoxyphenanthrene and 1.5 equivalents of *n*-butyl-lithium in 50 cc. of ether was refluxed for twenty hours. Subsequent to oxidation, as effected with the metalation product of 2-methoxyphenanthrene, there was obtained 0.23 g. or 30% of 2-hydroxy-3-methoxyphenanthrene (III) which melted at 171–172° after crystallization from methanol.

Anal. Calcd. for $C_{15}H_{12}O_2$: OCH_3, 13.83. Found: OCH_3, 14.29.

Fifty milligrams of 2-hydroxy-3-methoxyphenanthrene in acetone was methylated by methyl sulfate to give 30 mg. or 50% of 2,3-dimethoxyphenanthrene (V), melting at 132.5–133.5°, and shown to be identical with the two samples mentioned in the section on the oxidation of the metalation product of 2-methoxyphenanthrene.

3-Methoxy-2-acetoxyphenanthrene.—This compound, prepared like 2-methoxy-3-acetoxyphenanthrene, melted at 142–144° after crystallization from methanol.

Anal. Calcd. for $C_{17}H_{14}O_3$: OCH_3, 11.66. Found: OCH_3, 11.24.

A mixed melting point with 2-methoxy-3-acetoxyphenan-threne was depressed twenty degrees.

(18) Mosettig and Stuart, This Journal, 61, 1 (1939).

(19) Kindly provided by Dr. E. Mosettig.

(20) An adaptation of the procedure of Ivanoff, *Bull. soc. chim.*, 39, 47 (1926), for improving the yields of phenols by oxidation of RMgX compounds.

(21) Gilman and Schulze, This Journal, 47, 2002 (1925); Gilman and Jones, *ibid.*, 62, 1243 (1940).

(22) Mosettig and Burger, *ibid.*, 52, 2988 (1930).

Metalation of 9-Hydroxy- and 9-Methoxyphenanthrene.
—A mixture of 0.05 mole of n-butyllithium and 4.9 g. (0.025 mole) of 9-hydroxyphenanthrene in 150 cc. of a 1:1 ether–benzene medium was stirred and refluxed for twenty-four hours, and then carbonated. In addition to a recovery of 2 g. or 40% of the 9-hydroxyphenanthrene, there was obtained 0.56 g. or 10% of a 9-hydroxy-x-phenanthrenecarboxylic acid which melted with decomposition at 158–160° after crystallization from a benzene–acetone (4:1) mixture.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.70; H, 4.20; neut. equiv., 238., Found: C, 75.83; H, 4.35; neut. equiv., 242.

9-Methoxy-x-phenanthrenecarboxylic acid, prepared from 9-hydroxy-10-phenanthrenecarboxylic acid and methyl sulfate, melted at 197–199° after crystallization from benzene.

Anal. Calcd. for $C_{16}H_{12}O_3$: OCH_3, 12.30; neut. equiv., 252. Found: OCH_3, 12.16; neut. equiv., 244.

This methoxy acid did not depress the melting point of the higher melting methoxy acid obtained from 9-methoxyphenanthrene by metalation followed by carbonation.

A mixture of 0.170 mole of n-butyllithium and 8.0 g. (0.083 mole) of 9-hydroxyphenanthrene was stirred and refluxed for twenty hours. After cooling the mixture by an ice–salt-bath, bromine vapor in nitrogen was swept over the surface of the well-stirred suspension until there was a negative color test[21] for RM compound. Recrystallizations of the product, first from benzene–petroleum ether (b. p. 60–68°) and then from benzene, gave 15 mg. of a compound melting at 124–125.5°. This bromo compound when oxidized by chromic oxide in glacial acetic acid gave 5 mg. or 50% of phenanthrenequinone (mixed melting point). This apparently anomalous result warrants confirmation with a larger and analytically identified sample of the 9-hydroxy-x-bromophenanthrene.

From the carbonation of a reaction mixture of 0.025 mole of n-butyllithium and 4.2 g. (0.020 mole) of 9-methoxyphenanthrene in 100 cc. of ether which had been refluxed for sixteen hours, there were isolated two compounds. One of these obtained in 6 mg. quantity melted at 197–199° after crystallization from benzene and was shown by the method of mixed melting points to be identical with the methylation product of the hydroxy acid obtained from 9-hydroxyphenanthrene by metalation followed by carbonation. The other product, obtained in a 25 mg. quantity, melted at 111.5–113° after crystallization from benzene, and showed no depression in a mixed melting point determination with an authentic specimen of 9-methoxy-10-phenanthrenecarboxylic acid.[19] A mixture of the two methoxy acids obtained by us melted over the range 104–165°.

To a cold reaction mixture of 7.8 g. (0.0375 mole) of 9-methoxyphenanthrene and 0.04 mole of n-butyllithium in 100 cc. of ether which had been refluxed for twenty-two hours was added 0.04 mole of n-butylmagnesium bromide

and then oxygen until a negative color test was obtained. In addition to a 38% recovery of 9-methoxyphenanthrene, there was isolated 0.13 g. of what was probably 9-methoxy-10-hydroxyphenanthrene. These yellowish crystals melted at 94–95.5° after crystallization from petroleum ether.[23] The compound slowly decomposed on standing.

Anal. Calcd. for $C_{15}H_{12}O_2$: OCH_3, 13.84; Found: OCH_3, 13.67.

9-Hydroxyphenanthrene was prepared in accordance with the directions of Fieser and co-workers.[24] The methylation procedure of Stevens and Tucker[17] gave improved yields of the three methoxyphenanthrenes examined. The yield of 2-methoxyphenanthrene was 82% compared with 75%[25]; of 3-methoxyphenanthrene, 78% compared with 65%[25]; and of 9-methoxyphenanthrene, 78% of pure compound compared with 84% of crude with considerable loss in purification.[26]

Acknowledgments.—The authors are grateful to Dr. E. Mosettig for some mixed melting point samples, and to Mr. R. W. Leeper for other assistance.

Summary

Halogen–metal interconversion reactions have been effected with 2-, 3- and 9-bromophenanthrenes and n-butyllithium to give the corresponding phenanthryllithium compounds which were identified by carbonation to their respective acids:

$$RBr + n\text{-}C_4H_9Li \longrightarrow RLi \xrightarrow[\text{[HOH]}]{\text{[CO}_2\text{]}} RCO_2H.$$
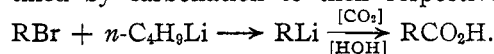
Metalation of 2-hydroxyphenanthrene and 2-methoxyphenanthrene, followed by carbonation, gave 2-hydroxy-3-phenanthrenecarboxylic acid and 2-methoxy-3-phenanthrenecarboxylic acid, respectively. Metalation of 3-hydroxyphenanthrene and 3-methoxyphenanthrene occurred in the 2-position.

However, metalation of 9-methoxyphenanthrene, followed by carbonation, yielded two products: 9-methoxy-10-phenanthrenecarboxylic acid and a 9-methoxy-x-phenanthrenecarboxylic acid. The latter acid was also obtained by reactions involving the metalation of 9-hydroxyphenanthrene. These are the first cases where metalation of a phenol or phenolic ether does not involve hydrogen in an *ortho* position.

AMES, IOWA   RECEIVED JULY 29, 1940

(23) Goldschmidt and Schmidt, *Ber.*, **55**, 3197 (1922), report the melting point as "coloring at 92° and melting sharply at 103°."

(24) Fieser, Jacobsen and Price, THIS JOURNAL, **58**, 2163 (1936).

(25) Werner, *Ann.*, **321**, 284, 306 (1902).

(26) Japp and Findlay, *J. Chem. Soc.*, **71**, 1122 (1897).