Summary

1. The rate and equilibrium for the addition of bromine to phenanthrene have been measured.

2. Evidence for a chain mechanism has been presented, as well as a method for the determination of its length.

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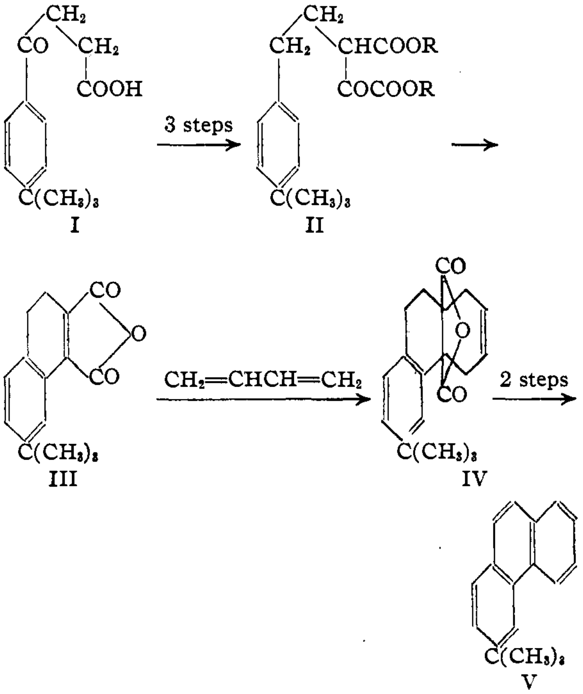
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Effect of Substituents on the Phenanthrene–Bromine Addition Reaction

BY LOUIS F. FIESER AND CHARLES C. PRICE

Following the observation[1] that the addition of bromine to phenanthrene proceeds to a measurable equilibrium at a conveniently measurable rate, it became of interest to investigate the effect of substituent groups in the terminal rings on the free energy and rate of the reaction. It seemed desirable to study compounds having substituents belonging to the three types distinguished by the nature of the directive influence which they exert on aromatic substitutions, and attention was directed first to 2- and 3-substituted phenanthrene derivatives since these are more readily available than the 1- and 4-isomers. As representative compounds with meta-directing groups the 2- and 3-carboxylic esters of phenanthrene were selected and found satisfactory. Halogen atoms constitute a special class of substituent since they retard substitution in the benzene ring like meta groups yet direct to the ortho–para positions, but of the compounds desired only 3-chlorophenanthrene[2] had been described at the time our work was undertaken. The 2- and 3-halophenanthrenes, however, were conveniently obtained from the acetyl compounds[3] through the oximes, acetylamines and amines, a method which has been reported by Bachmann and Boatner[4] in a preliminary communication published since the completion of our work.

It was a more difficult matter to find suitable 2- and 3-phenanthrene derivatives having ortho–para directing groups of the type that facilitate aromatic substitutions. A too powerfully directing group would lead to substitution in the terminal nucleus rather than 9,10-addition, and this apparently is the case with the methoxy- and acetylamino-phenanthrenes for they rapidly absorb more than one mole of bromine irreversibly in carbon tetrachloride solution. The same observation was made with 3-ethylphenanthrene, and it is possible that in this case the principal reaction is a side-chain substitution. The phenanthryldimethyl carbinols were investigated but they proved to be too unstable. Finally the tertiary butyl compounds were synthesized and found entirely satisfactory for the purpose. 3-*ter.*-Butylphenanthrene (V) was obtained by the synthetic method of Fieser and Hershberg[5] starting with the keto acid I resulting from the condensation of *ter.*-butylbenzene with succinic anhydride.



The structure was established by conversion to *p*-*ter.*-butylbenzoic acid and terephthalic acid. The addition of butadiene to III and the remaining steps all proceeded very satisfactorily, affording

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[1] Price, THIS JOURNAL, **58**, 1834 (1936).

[2] Sandqvist, *Ann.*, **396**, 116 (1909).

[3] Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

[4] Bachmann and Boatner, *ibid.*, **58**, 857 (1936).

[5] Fieser and Hershberg, *ibid.*, (a) **57**, 1851 (1935); (b) **57**, 2192 (1935).

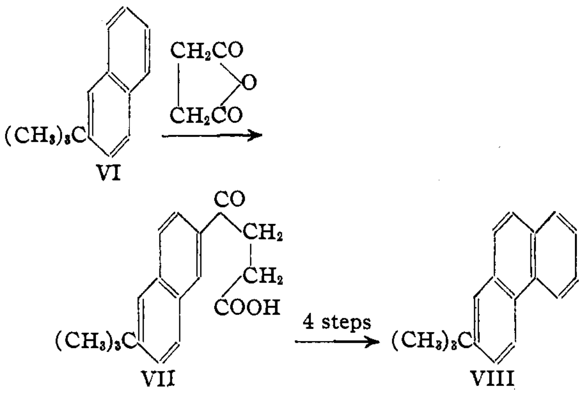
TABLE I

EQUILIBRIUM AND RATE DATA FOR THE PHENANTHRENE–BROMINE-ADDITION REACTION FOR VARIOUS PHENANTHRENE DERIVATIVES IN CARBON TETRACHLORIDE SOLUTION AT 25 AND 36°

Compound	$K_{25°}$	$K_{36°}$	$k_{25°}$	$k_{36°}$	$-\Delta F_{25°}$ (cal.)	$-\Delta H$ (cal.)	ΔS (cal./deg.)
2-Carbethoxyphenanthrene	168	88	2.0–7.0	3–7	3070	10,400	24.6
3-Carbethoxyphenanthrene	93	59	1.5–3.0	1.5–5	2690	7,200	14.9
2-Carbomethoxyphenanthrene	167	81	0.4–0.7	0.5–1	3030	11,300	27.8
3-Carbomethoxyphenanthrene	129	63	3–8	0.75–1.25	2880	11,250	28.2
2-Chlorophenanthrene	159	54	0.02–0.05	0.015–0.025	3000	16,900	46.6
3-Chlorophenanthrene	170	67	0.3–0.7	0.5–1.5	3040	14,300	37.7
2-Bromophenanthrene	152	59	0.02–0.05	0.02–0.05	2980	14,800	39.6
3-Bromophenanthrene	152	69	....	0.3–1.0	2990	12,800	32.9
Phenanthrene	230	148	7–11	7–11	3220	7,350	13.8
2-*ter.*-Butylphenanthrene	320	262*	1–4	2–5	3420	3,350	0
3-*ter.*-Butylphenanthrene	467	191*	7–11	5–7	3640	12,900	31.1

(* 37.4°.)

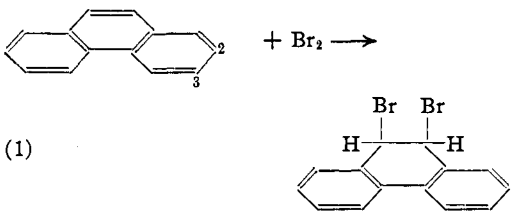
an easily purified hydrocarbon. The synthesis of the 2-isomer was patterned after Haworth's syntheses and based upon his observation[6] that in nitrobenzene solution succinic anhydride condenses with β-methyl- and β-isopropyl-naphthalene in the 6-position. β-*ter.*-Butylnaphthalene was found to react in the same way, giving the keto acid VII. On reduction, cyclization and



conversion to an aromatic hydrocarbon, the product was found to be a phenanthrene derivative isomeric with 3-*ter.*-butylphenanthrene and yielding on oxidation an ortho quinone with the substituent still intact, hence a *ter.*-butyl-9,10-phenanthrenequinone. Theoretically VI could give rise to 2-, 3- or 9-*ter.*-butylphenanthrene, and since the last two structures are eliminated the substance obtained is the 2-isomer and the keto acid (VII) has the structure shown.

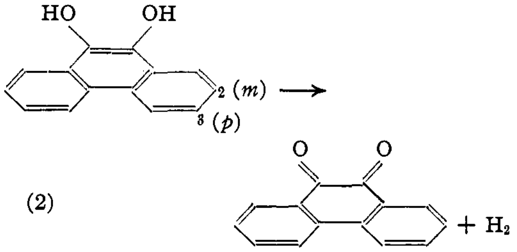
The bromine-addition reaction was studied in carbon tetrachloride solution by the method employed for phenanthrene[1] and the results are summarized in Table I. On comparing the equilibrium constants at 25 and 36° with the values for phenanthrene it is seen that the constants at the two temperatures are roughly parallel for the pairs of isomers except in the case of the two alkyl compounds. It is quite interesting that halogen substituents fall into line with the typically meta-directing carboxylate groups in decreasing the free energy of the bromine-addition, while an alkyl group has just the opposite effect. This relationship is exactly that found for the effect of groups of these three types on the oxido-reduction potentials of quinone-hydroquinone systems,[7] and it is of interest to compare the reactions:

(1)



$-\Delta F_{25°}$ = 3220 cal.

(2)



$-\Delta F_{25°}$ = 21,736 cal.[8]

As applied to the oxidation of a hydroquinone (Reaction 2), a rule previously stated[7] in terms of potentials may be phrased as follows: groups which facilitate substitution in the benzene ring increase the free energy of oxidation, while those which retard benzene-substitution, including meta-directing groups and halogen atoms, have the opposite influence. It is clear from the present re-

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[6] Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932).

[7] Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

[8] From the normal potential in 95% alcoholic solution, Fieser, *ibid.*, **51**, 3101 (1929).

sults that the rule applies equally well to Reaction 1. In each case the reaction involves the conversion of the central, benzenoid ring into a dihydrobenzenoid nucleus, and substituents in a terminal ring exert similar influences in the two processes. The free energy change in the bromine-addition is much less than in the oxidation, but a substituent has nearly the same proportionate influence in each case, as can be seen from the comparisons given in Table II. Although the effect of a 3-*ter.*-butyl group on the free energy of oxidation is not known, it can be inferred from other data[7,8] that such a group probably would increase the free energy change to about twice the extent that a bromine atom decreases it. This again corresponds to the findings regarding Reaction 1.

TABLE II

EFFECT OF SUBSTITUENTS IN CALORIES ON $-\Delta F$

Substituent	Reaction 1	Reaction 2
3-Bromo	230 (7.1%)	1292 (5.9%)
3-Carbomethoxy	340 (10.0%)	2677 (12.3%)

With regard to the effect of the position of the substituent in the phenanthrene nucleus, it has been observed[8] in the case of Reaction 2 that the effect of a group in either the positive or negative direction is greater when it is situated in the 3-position para to the 10-hydroxyl group than when it is located at the meta position 2. The present results are hardly extensive enough to show whether or not this is true also of Reaction 1. With the halogen compounds the differences in the values of $-\Delta F$ for the isomers are too slight to be significant. The ester groups are invariably more effective in the 3-position, and the differences are quite noticeable. Considering the free energy changes at 25°, the same relationship holds for the *ter.*-butyl group, but in this case there is a curious reversal at the higher temperature and more data will be required to establish the analogy.

Comparing the rate constants for the bromine-addition to the substituted phenanthrenes (Table I), it may be said that there is no striking deviation from the behavior of phenanthrene, and no significant difference between isomers, except in the case of the halogen compounds. A halogen atom at either the 2- or 3-position definitely retards the addition reaction, and there is a decided difference between the isomers. The rate constants for 2-bromo- and 2-chlorophenanthrene are only about one-fortieth as great as the constants for the 3-isomers. Considering that the 2-position is meta to one of the unsaturated carbon atoms concerned in the addition reaction while a 3-substituent occupies a para position with respect to this group, it may be said that halogen is somewhat inhibitory to the addition of bromine in any event but that it exerts a pronounced and specific inhibiting influence when in the meta (2-) position. This suggests a possible explanation of the peculiar fact that halogen atoms stabilize the benzene ring like the common meta-directing groups but nevertheless direct substituents into the ortho-para positions. In the present study halogen is classed with the meta-type groups with respect to its effect on the equilibrium (stabilizing effect) but is found to differ from other groups in specifically decreasing the rate of a reaction at a center with respect to which it occupies the meta position.

Experimental Part[9]

The phenanthroic esters were prepared according to Mosettig and van de Kamp[3] and the melting points were as follows: 2-methyl 95–96°, 2-ethyl 72.5–73.5°, 3-methyl 93.5–94.5°, 3-ethyl 55–56°. Incidentally, 3-acetophenanthrene on purification through the picrate was found to melt at 73.5–74.5°; picrate, m. p. 123–125°. In the hypochlorite oxidation of the acetophenanthrenes the time of reaction was shortened greatly by providing vigorous mechanical stirring. 3-Ethylphenanthrene[3] was purified through the picrate, m. p. 120–122°, and distilled. The halophenanthrenes employed had the following melting points: 2-chloro 86.5–87.5°, 2-bromo 97–98°, 3-chloro 82–83°, 3-bromo 82–83°. In view of the announcement of Bachmann and Boatner[4] the preparations and analyses will be omitted, but it may be noted that 2-acetophenanthrene-oxime (m. p. 193–195°, crystallized with excess hydroxylamine) and the 3-isomer were obtained in 83–95% yield, rearranged with phosphorus pentachloride in dry ether and converted to the phenanthrylamine hydrochlorides in about 70% yield. The Sandmeyer reaction proceeded best (45% yield) when the diazonium salt was added to the boiling cuprous halide solution.

2-Phenanthryldimethyl carbinol was prepared by adding a solution of 2-acetophenanthrene in benzene to an ethereal solution of methylmagnesium iodide and refluxing. On allowing a solution of the crude product (80% yield) in petroleum ether to evaporate at room temperature the substance was deposited as long silky needles, m. p. 90–92°, dec., and as cubes, m. p. 97–99°, dec.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.44; H, 6.95. Found: (needles) C, 86.66; H, 6.85; (cubes) C, 86.12; H, 6.94.

3-Phenanthryldimethyl carbinol was obtained, after purification through the picrate, as an oil which crystallized from petroleum ether in a bath of solid carbon dioxide and alcohol but melted again at room temperature. The

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[9] Analyses by Mrs. G. M. Wellwood.

picrate separated from methyl alcohol as bright orange crystals, m. p. 107–110°, dec.

Anal. Calcd. for $C_{17}H_{16}O \cdot C_6H_3O_7N_3$: C, 59.32; H, 4.13. Found: C, 59.50; H, 4.11.

On recrystallization from alcohol the melting point rose eventually to 160–163°, dec., and apparently dehydration had occurred giving 3-isopropenylphenanthrene picrate (calcd. C, 61.7; H, 3.8. Found: C, 62.5; H, 3.7).

Synthesis of 3-*ter*.-Butylphenanthrene

β-(*p*-*ter*.-Butylbenzoyl)-propionic Acid (I).—*ter*.-Butylbenzene (17 g.) was added slowly to a mixture of succinic anhydride (13 g.), aluminum chloride (36 g.), and carbon bisulfide (100 cc.), and after refluxing for one hour the mixture was cooled and decomposed with ice and hydrochloric acid. After removing the solvent with steam the product solidified (20 g.) and on crystallization from 50% acetic acid it was obtained as colorless crystals, m. p. 121–122°; yield 16.5 g. (55%). The substance crystallizes from dilute alcohol as lustrous plates and from benzene–ligroin as large cubes; both forms melt at 121–122°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.73. Found: C, 71.46; H, 7.30.

The acid was converted by oxidation with potassium hypochlorite into *p*-*ter*.-butylbenzoic acid, m. p. 165–166°, corr., and this with dilute nitric acid gave terephthalic acid, identified as the dimethyl ester, m. p. 140.5–141°, corr., by comparison with an authentic sample.

γ-(*p*-*ter*.-Butylphenyl)-butyric acid was obtained in 72% yield from the keto acid by Martin's modification[10] of the Clemmensen method as already reported.[10] After refluxing for fifteen hours the product was collected and dried in ether and distilled, b. p. 164–167° (5 mm.), m. p. 57–60°. Recrystallized from petroleum ether the acid formed small crystals, m. p. 59.5–60.5°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.30; H, 9.17. Found: C, 76.30; H, 9.04.

The **ethyl ester** was conveniently prepared by distilling off the toluene at the end of the reduction, extracting with ether, esterifying the crude acid with absolute alcohol and hydrogen chloride, and distilling the ester. It was obtained as a colorless liquid, b. p. 145–147° (5 mm.), in 70% yield.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.41; H, 9.68. Found: C, 77.38; H, 10.19.

7-*ter*.-Butyl-Δ^1-dihydronaphthalene-1,2-dicarboxylic Anhydride (III).—Ethyl γ-(*p*-*ter*.-butylphenyl)-butyrate (63 g.) was condensed with ethyl oxalate in the presence of sodium ethylate by the procedure of Fieser and Hershberg[5a] and the crude oxalyl derivative (II), obtained as a light reddish oil after removal of the ether at diminished pressure, was cyclized by stirring a mixture of the oil with twenty parts by volume of 80% sulfuric acid at room temperature, heating the deep red solution to 60° and maintaining this temperature for ten minutes. The anhydride separated as a yellow solid which was collected after cooling on a sintered glass funnel and washed with fresh acid and with water. The yield of microcrystalline material was 55 g. (85%). Crystallized from benzene–ligroin the anhydride formed nearly colorless, flat needles, m. p. 143–145°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.97; H, 6.28. Found: C, 75.36; H, 6.28.

The sulfuric acid liquor on standing deposited a second substance (0.8 g.) which after two crystallizations formed faintly yellow needles, m. p. 174–175°. The substance has the same composition as the chief reaction product (found: C, 75.19, 75.19; H, 6.33, 6.25) and it may arise from a small amount of an isomer present in the starting material.

7-*ter*.-Butylnaphthalene-1,2-dicarboxylic anhydride was obtained in good yield by heating the dihydro compound with the calculated amount of sulfur at 330–340° for one hour and distilling the product. Long, pale yellow needles, m. p. 146.5–147.5°, were obtained from benzene–ligroin.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.71; H, 5.70.

6-*ter*.-Butyl-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic anhydride (IV) was obtained by heating a mixture of 12.2 g. of the anhydride and 31.8 g. of butadiene at 150° for thirty-six hours. On distillation at 1 mm. pressure (bath at 240–260°) there was obtained 12.8 g. of colorless material which fluoresced bright blue in ultraviolet light. Crystallized from benzene–ligroin it formed stout, colorless needles, m. p. 85.5–86.5°; yield 10 g. (68%).

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.36; H, 7.16. Found: C, 77.43; H, 7.20.

3-*ter*.-Butylphenanthrene.—The diene addition product (5 g.) was heated with 10 g. each of potassium hydroxide and water in the manner described,[5b] and after driving off the water the bath temperature was brought to 330–360°, when 2.5 g. (about 65%) of hydrocarbon collected as a colorless distillate (oil). A portion of the distillate (2.2 g.) was heated under nitrogen with 4 g. of selenium, added in portions, for thirty-six hours and the product was extracted with petroleum ether and vacuum distilled from a small bit of sodium. The pale yellow distillate soon solidified, m. p. 49–52°, yield 1.5 g. The hydrocarbon crystallized from alcohol as colorless, centimeter-long, prismatic needles fluorescing bright blue in ultraviolet light, m. p. 54–55°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.24; H, 7.76. Found: C, 92.30, 92.00; H, 7.55, 7.99.

The **picrate**, once recrystallized from alcohol, formed orange needles, m. p. 142–143°.

Anal. Calcd. for $C_{18}H_{18} \cdot C_6H_3O_7N_3$: C, 62.17; H, 4.58. Found: C, 61.79; H, 4.26.

The **quinone** was obtained by heating the hydrocarbon with chromic anhydride in acetic acid solution at 80–90° for one hour, the product separating as bright orange needles on cooling (77% yield). Recrystallized from alcohol it formed slender orange needles, m. p. 186–187°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.51; H, 6.15.

Synthesis of 2-*ter*.-Butylphenanthrene

β-*ter*.-Butylnaphthalene.—A mixture of 330 g. of naphthalene and 251 g. of *ter*.-butyl chloride was warmed at

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[10] Martin, This Journal, 58, 1438 (1936).

50–60° until the solid had dissolved and 10 g. of aluminum chloride was added in small portions with stirring in about one and one-half hours. The reaction was largely over when about half of the aluminum chloride had been added. After a further half-hour of stirring the material was washed and dried in benzene and distilled. About 100 g. of naphthalene came over up to 140° (12 mm.) and the main product distilled at 119–135° (6 mm.). Redistillation gave 140 g. (30%) of β-*ter.*-butylnaphthalene as a colorless oil, b. p. 127–131° (9 mm.), picrate, m. p. 99.5–100.5°. The picrate of the hydrocarbon obtained by other methods is reported to melt at 102–103°[11] and at 96°.[12]

Di-*ter.*-**butylnaphthalenes.**—The combined higher-boiling fractions from the above preparation on redistillation gave 100 g. of a fraction boiling at 150–170° (10 mm.) and promptly solidifying. This apparently consisted largely of a mixture of the two di-*ter.*-butylnaphthalenes described by Gump,[13] and in a preliminary examination it was found that the higher-melting isomer can be isolated easily by two crystallizations from methyl alcohol: thick, lustrous plates, m. p. 146–147°. As this isomer does not form a picrate in alcoholic solution whereas the lower-melting hydrocarbon does, the latter can be isolated easily from the mother liquor or from the original mixture as the picrate. This picrate was obtained as beautiful orange needles, m. p. 155.5–156.5°, but it was not analyzed successfully. The hydrocarbon regenerated from the purified picrate formed fine cottony needles from alcohol; it melted unsharply at 86–90° but had the expected composition.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: (146–147°) C, 90.14; H, 10.39; (86–90°) C, 90.17; H, 9.92.

A quinone was obtained by refluxing a solution of the higher-melting hydrocarbon in glacial acetic acid with chromic anhydride for twenty minutes. It was purified with Norite in ether solution and crystallized from alcohol; slender, bright yellow needles, m. p. 83.5–84.5°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.22. Found: C, 79.98; H, 8.15.

β-(**6**-*ter.*-**Butylnaphthoyl-2**)-**propionic acid (VII)** was prepared by adding with stirring 140 g. of β-*ter.*-butylnaphthalene and 66 g. of succinic anhydride to a solution of 226 g. of aluminum chloride in 1.5 liters of nitrobenzene at 0°. After eight hours at 0° and one day at room temperature ice and hydrochloric acid were added and the solvent removed with steam. The dark brown mass remaining after decanting the aqueous liquor was treated with a small quantity of ether, as this dissolved a dark oil and left a fairly clean solid (92 g.). This was dissolved in glacial acetic acid and the solution was diluted with hot water until cloudy and treated with a liberal quantity of Norite. The filtered solution deposited glistening, colorless needles, m. p. 148–150°; total yield, 80 g. (37%).

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.07; H, 7.04. Found: C, 76.02; H, 7.11.

γ-(**6**-*ter.*-**Butylnaphthyl-2**)-**butyric Acid.**—The above keto acid was largely unchanged when submitted to reduction by the usual Clemmensen method or with added toluene (thirty hours) but, as already noted,[10] the reaction proceeded smoothly by Martin's method using toluene and a small amount of acetic acid, yield crude 78%. A portion of the acid was purified through the methyl ester, b. p. 185–187° (6 mm.), and after saponification crystallized from petroleum ether. It separated as long, slender needles which soon changed in part at least into short, stout needles. Apparently neither form was obtained as a pure individual, for the melting points were unsharp and varied from 87 to 95°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.94; H, 8.22. Found: C, 79.86; H, 8.36.

7 - *ter.* - **Butyl** - **1** - **keto** - **1,2,3,4** - **tetrahydrophenanthrene.**—The above acid (20 g.) was warmed gently with purified thionyl chloride and the mixture was then heated on the steam-bath and the excess reagent removed by water pump suction. The acid chloride was dissolved in 150 cc. of carbon bisulfide and treated at 0° with 14.7 g. of aluminum chloride. The mixture was allowed to come to room temperature, refluxed for fifteen minutes, and worked up as usual. After distillation the product (12 g., 65%) remained as a pale yellow, viscous oil, and it was characterized as the **picrate**, which formed yellow needles from alcohol, m. p. 107–108°.

Anal. Calcd. for $C_{18}H_{20}O \cdot C_6H_3O_7N_3$: C, 59.85; H, 4.82. Found: C, 59.75; H, 5.01.

2-*ter.*-**Butylphenanthrene.**—The cyclic ketone (3.6 g.) was reduced by refluxing for fifteen hours with 17 g. of amalgamated zinc, 35 cc. of constant boiling hydrochloric acid, and 4 cc. of toluene, and the crude product was heated at 320–350° with 9 g. of selenium, added in portions, for sixty hours. The resulting hydrocarbon was extracted with petroleum ether, distilled in vacuum from a small piece of sodium, and the solid distillate (1.5 g.) crystallized twice from alcohol (0.85 g.). The hydrocarbon formed colorless, pearly plates, m. p. 99–100°, showing a brilliant purple fluorescence in ultraviolet light.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.24; H, 7.76. Found: C, 92.38; H, 7.71.

The **picrate** forms orange needles, m. p. 130–131°.

Anal. Calcd. for $C_{18}H_{18} \cdot C_6H_3O_7N_3$: C, 62.17; H, 4.58. Found: C, 62.29; H, 4.47.

The **quinone**, purified through the bisulfite addition product and crystallized from alcohol, formed bright orange needles, m. p. 129–130°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.62; H, 6.34.

Summary

Carboxylic ester groups and halogen atoms in the 2- and 3-positions of phenanthrene decrease the free energy of the 9,10-addition of bromine, while the *ter.*-butyl group has the opposite effect. The results parallel those obtained in the study of the free energy of oxidation of 9,10-phenanthrenehydroquinones and there is a correlation between the observed effects of the groups and their influence in retarding or facilitating sub-

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[11] Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930).

[12] Wegscheider, *Monatsh.*, **5**, 237 (1884).

[13] Gump, THIS JOURNAL, **53**, 380 (1931).

stitutions in the benzene ring. Of further bearing on the latter problem is the observation that halogen atoms in the 2(meta)-position specifically decrease the reaction rate. 2- and 3-*ter.*-butylphenanthrene were synthesized for use in the investigation.

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Studies of the Reducing Action of Mercury. III. Hydrogen Peroxide Formation and the Copper-Catalyzed Autoxidation of Quinquivalent Molybdenum and Other Strong Reductants in Acid Solution

BY W. M. MURRAY, JR., AND N. HOWELL FURMAN

The first paper[1] of this series dealt with the formation of hydrogen peroxide when mercury and dilute hydrochloric acid are shaken in the presence of air. The second article[2] discussed the use of the mercury reductor in a new method for the determination of molybdenum and mention was made of the catalytic action of copper on the autoxidation of quinquivalent molybdenum.

It will be the object of this work to give data which show more clearly just what takes place in the mercury reductor when heavy metal ions are present and how it is possible to use the mercury reductor as an analytical tool even though the formation of hydrogen peroxide in the reductor is possible. Also, the question of the autoxidation of quinquivalent molybdenum solutions and the copper catalysis of this and of the analogous autoxidations of stannous, titanous and uranous solutions will be discussed more fully.

Hydrogen Peroxide in the Mercury Reductor.—Some of the work on the action of metallic mercury as a reducing agent was done by Schaffhaütl[3] and Carnegie,[4] although neither of these investigators undertook the subject from a quantitative standpoint. Later Borar[5] studied the stoichiometry of the reaction between mercury and potassium permanganate, potassium dichromate, ferric chloride and cupric sulfate.

McCay and Anderson[6] proposed the mercury reductor for use in the quantitative determination of ferric salts, and later they[7] studied the reduction of vanadic acid solutions by mercury. Finally, McCay[8] worked on the reduction of antimonic acid solutions by mercury as a quantitative method for determining antimony.

At present, then, mercury reduction has been proposed as a quantitative and efficient method for the determination of iron, vanadium, antimony and molybdenum. The reduction by mercury of solutions of these elements is always carried out in the presence of hydrochloric acid. It appears rather paradoxical that mercury can be used for the quantitative reduction of the above substances when we recall that mercury and hydrochloric acid will react rapidly with oxygen to form large amounts of hydrogen peroxide. The explanation of this seems to be largely a matter of competing rates, except in the case of antimony.

Solutions of iron, molybdenum, and vanadium salts are known to be good catalysts for the decomposition of hydrogen peroxide. It is then evident that if we shake a mixture of mercury and hydrochloric acid in the presence of oxygen and add small amounts of iron, vanadium or molybdenum salts to the mixture, the hydrogen peroxide should be decomposed catalytically by the heavy metal ions present. There would in such a case be two competing reactions: (a) the formation of hydrogen peroxide in the reaction between mercury, hydrochloric acid, and oxygen; (b) the catalytic decomposition of the hydrogen peroxide by the heavy metal ion. If reaction (a) is faster than reaction (b) we will be able to detect hydrogen peroxide in the mixture, but if step (a) is the slow one, then all the peroxide will be decomposed and will not be evident in the solution. However, the rate of reaction (b) will depend to some extent on the concentration of the heavy metal ion and the rate of its reduction by mercury since the decomposition of hydrogen peroxide by these ions is very probably an alternate oxidation and reduc-

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(1) Furman and Murray, THIS JOURNAL, **58**, 429 (1936).
(2) Furman and Murray, *ibid.*, **58**, 1689 (1936).
(3) Schaffhaütl, *Ann.*, **44**, 25 (1842).
(4) Carnegie, *J. Chem. Soc.*, **53**, 468 (1888).
(5) Borar, *ibid.*, **99**, 1414 (1911).
(6) McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).
(7) McCay and Anderson, *ibid.*, **44**, 1018 (1922).
(8) McCay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).