a solution of 0.85 g. of trimethyl isocyanurate in 200 cc. of benzene (dried over sodium) added slowly. The mixture was heated on a boiling water-bath for four hours, the ether gradually being distilled off on a descending condenser and the remaining solution finally refluxed. The material was decomposed and extracted as above. The residue crystallized on prolonged standing in the ice-box. It was recrystallized from benzene and from methanol; m. p. 161°, mixed m. p. with substance VIIA, 135°; with triphenylcarbinol, 161°.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19; mol. wt., 260.1. Found: C, 87.46; H, 6.36.

Reaction of Substance VIIA with Grignard Reagent.—C_6H_5MgBr was prepared from 0.48 g. of magnesium and 3.2 g. of bromobenzene in 100 cc. of dry ether and a solution of 0.8 g. of substance VIIA in 100 cc. of ether slowly added. After refluxing for two hours, the material was worked up as above. The oily ether residue crystallized on addition of petrolic ether and was recrystallized from benzene; m. p. and mixed m. p. with substance VIIA, 159°. From the mother liquors a small amount of triphenylcarbinol could be obtained.

Bromination of VIIA.—To 250 mg. of substance dissolved in 1 cc. of glacial acetic acid, 4.0 cc. of an 8% bromine solution in glacial acetic acid was added slowly. A red crystalline precipitate formed, which was filtered and washed with ether. During this procedure hydrogen bromide is lost and the color changes to dark yellow. Recrystallization from glacial acetic acid; yield 80%; m. p. 196°. The substance is very soluble in methanol, ethanol, soluble in hot glacial acetic acid and chloroform; insoluble in ether, petrolic ether, water.

Anal. Calcd. for $C_{12}H_{14}O_2N_3Br_3$: C, 30.52; H, 2.99; N, 8.90; Br, 50.81; mol. wt., 471.88. Found: C, 30.79; H, 3.09; N, 8.62; Br, 50.63.

Bromination of the Ethyl Derivative VIIB, as above.—The resulting tribromo derivative is soluble in water and organic solvents, except ether and petrolic ether, m. p. 128°.

Anal. Calcd. for $C_8H_{14}O_2N_3Br_3$: Br, 56.56; mol. wt., 423.88. Found: Br, 56.42.

Bromination of the Propyl Derivative VIIC.—Preparation and solubilities were as above, m. p. 151°.

Anal. Calcd. for $C_9H_{16}O_2N_3Br_3$: Br, 54.75; mol. wt., 437.90. Found: Br, 54.52.

Iodination of 1,3,5-Trimethyl-2-propyl-2-hydroxy-4,6-dioxohexahydrotriazine, VIIC.—Fifty milligrams of substance VIIC was dissolved in a few drops of chloroform and 2 cc. of a 12% solution of iodine in chloroform was added. On standing overnight the triiodo compound crystallized. The same substance was also obtained with better yield (90%) from the corresponding tribromo derivative VIIIC by shaking 50 mg. with a solution of 1 g. of potassium iodide in 3 cc. of water. Recrystallization from hot glacial acetic acid; m. p. 112–115°; soluble in methanol and ethanol.

Anal. Calcd. for $C_9H_{16}O_2N_3I_3$: I, 65.75; mol. wt., 578.90. Found: I, 64.92.

Summary

Trimethyl isocyanurate reacts with Grignard compounds to form 1,3,5-trimethyl-2-alkyl-(or aryl)-2-hydroxy-4,6-dioxohexahydrotriazines, into which three atoms of bromine or iodine may be introduced.

NEW YORK, N. Y. RECEIVED JULY 15, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

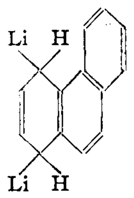
The Addition of Alkali Metals to Phenanthrene

BY ALLENE JEANES[1] AND ROGER ADAMS

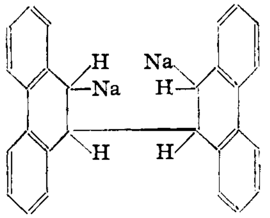
The addition of alkali metals to aromatic compounds was first studied intensively by Schlenk and Bergmann.[2] Since 1928 much interest has been shown in such compounds and they have proved to be valuable intermediates in synthetic work not only from a scientific but also from a practical standpoint.[3]

This communication contains a discussion of Schlenk's results on the addition of alkali metals to phenanthrene and a description of a detailed study of dialkaliphenanthrenes and their derivatives made in this Laboratory.

Schlenk[2] reported that lithium added to phenanthrene in the 1,4-positions (I). On the other hand, he showed that sodium reacted to form a substance reported as the 9,9′-biphenanthryl (II).



I



II

Ziegler[3a] obtained a compound corresponding to Schlenk's biphenanthryl (II) by the reaction

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[1] Abstract of a thesis submitted in partial fulfilment of the requirement for the degree of Doctor of Philosophy in Chemistry.

[2] Schlenk and Bergmann, *Ann.*, **463**, 84 (1928); see also Berthelot, *Ann. chim.*, [4] **12**, 155 (1867).

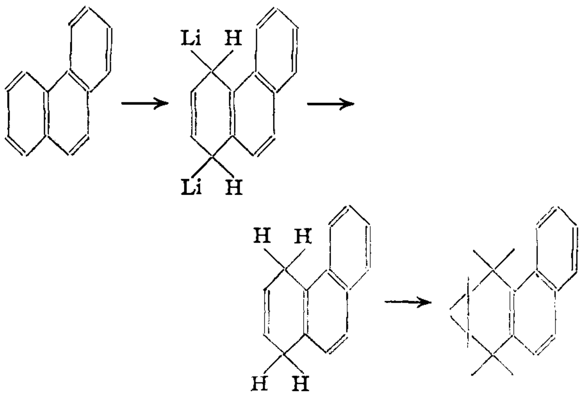
[3] (a) Ziegler and Bäher, *Ber.*, **61**, 253 (1928); (b) Ziegler and Crössmann, *ibid.*, **62**, 1768 (1929); (c) Ziegler and Wollschitt, *Ann.*, **479**, 123 (1930); (d) Ziegler, *Angew. Chem.*, **49**, 455 (1936); (e) N. D. Scott, U. S. Patents, 2,054,303, 2,019,832, 2,023,793, 2,027,000; (f) N. D. Scott, Walker and Hansley, THIS JOURNAL, **58**, 2442 (1936).

between phenylisopropylpotassium and phenanthrene. He accepted the formula proposed by Schlenk with the reservation that conclusive proof of its correctness was lacking. Scott[3e] added sodium to phenanthrene and carbonated the product; he isolated a dicarboxylic acid which he assumed to be a 1,4-dicarboxy-1,4-dihydrophenanthrene on the basis of Schlenk's results.

All experimental and theoretical evidence leads to the conclusion that the 9,10-positions in phenanthrene are far more active to additive reagents than any others in the molecule. Moreover, Schlenk demonstrated that both sodium and lithium add in the 9,10-positions in 9,10-diphenylphenanthrene, for he was able to decompose the products with alcohol to give 9,10-diphenyl-9,10-dihydrophenanthrene and by carbonation to give the anhydride of 9,10-dicarboxy-9,10-diphenyl-9,10-dihydrophenanthrene.

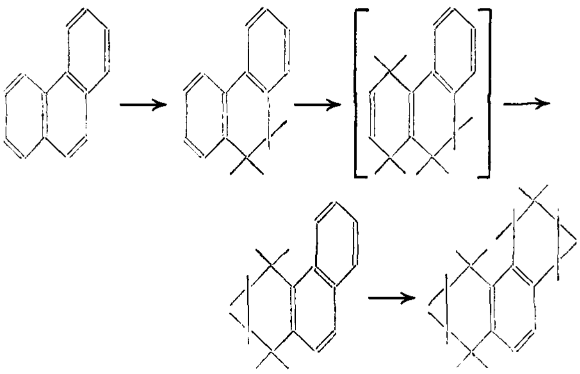
That Schlenk misinterpreted his experimental results in regard to compound I is shown from the consideration of Schroeter's work that follows, and that he obtained neither compound I nor II is demonstrated definitely by experiments reported here.

Schlenk allowed lithium to react in diethyl ether with phenanthrene for eight days. On decomposing the product with alcohol, he obtained a colorless oil which was purified and shown to be a dihydrophenanthrene. Upon catalytic reduction of this dihydro product, two atoms of hydrogen were absorbed with the formation of a tetrahydro derivative. His explanation of these reactions is shown below.



Schlenk assumed that if the lithium had added 9,10-, the resulting dihydrophenanthrene would not absorb two atoms of hydrogen.

However, Schroeter[4] has demonstrated that the catalytic hydrogenation of phenanthrene occurs in three stages and established the structure of each product by synthesis.



The 9,10-positions take up the first two atoms of hydrogen. After the addition of the next two in one of the terminal rings a predictable rearrangement occurs in which two hydrogens, one from the 9- and one from the 10-position transfer to the partially hydrogenated terminal ring with the formation of 1,2,3,4-tetrahydrophenanthrene.

The boiling point of the dihydrophenanthrene of Schlenk was identical with that reported by Schroeter, 168–169° (15 mm.)

The boiling point reported by Schlenk for an admittedly impure sample of the tetrahydrophenanthrene, however, was about 15° lower than that reported by Schroeter.

In this investigation a distinct experimental advantage has been available that was unknown to Schlenk. This is the discovery made by Scott[3e] that certain solvents of higher oxygen content than diethyl ether accelerate the addition of alkali metals to unsaturated linkages. By use of such a solvent experiments were carried out on the reaction of sodium, potassium and lithium with phenanthrene. From these it has been found that 1,4-addition of lithium to phenanthrene does not occur, and that each of the alkali metals used adds in the 9,10-positions.

Ethylene glycol dimethyl ether is the solvent that was utilized to bring about the addition of sodium, potassium and lithium to phenanthrene. In each case *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene was isolated. As a by-product in some of the reactions an acid was formed the properties of which correspond exactly to those of Schlenk's 10,10′-dicarboxy-9,9′,10,10′-tetrahydro-9,9′-biphenanthryl. This product has been proved to be 9-fluorenecarboxylic acid by comparison of its properties with those of the authen-

[4] Schroeter, Müller and Huang, *Ber.*, **62**, 645 (1929).

tic acid described by previous investigators and by its characteristic conversion to fluorene and fluorenone.

The 9-fluorenecarboxylic acid was obtained when the phenanthrene used was natural material purified by ordinary methods, which are not designed specifically to remove all the fluorene. Synthetic phenanthrene and phenanthrene that has been repeatedly fused with sodium and then distilled, yield no 9-fluorenecarboxylic acid. When fluorene is present, dialkali phenanthrenes react with it to give an alkali fluorene which upon carbonation forms 9-fluorenecarboxylic acid. It is thus obvious that the acid reported by Schlenk as 10,10′-dicarboxy-9,9′,10,10′-tetrahydro-9,9′-biphenanthryl was not obtained by him and that his product was formed merely as a by-product due to impurity in the initial phenanthrene. The same substance, reported by Ziegler,[3a] was also formed undoubtedly from the fluorene impurity in the phenanthrene.

Since the formation of 9-fluorenecarboxylic acid as just described is a secondary reaction, it might be expected to occur slowly. The validity of this is attested by the observation that the amount of 9-fluorenecarboxylic acid formed during the carbonation of alkali phenanthrenes increased, up to a certain limit, as the length of time the alkali phenanthrene was left uncarbonated in the reaction mixture increased. This condition has existed in the cases of (1) Schlenk's reaction of sodium on phenanthrene in diethyl ether; (2) lithium reacting with phenanthrene in ethylene glycol dimethyl ether; in both (1) and (2) the reaction was allowed to run many hours before carbonation; (3) carbonation of sodium phenanthrene in ethylene glycol dimethyl ether at a rate slower than that normally used to produce *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene; and (4) in all carbonation reactions using potassium and phenanthrene, in which the metal addition product forms with marked rapidity. In each of these cases 9-fluorenecarboxylic acid was obtained in significant amounts.

In accordance with these facts, proof of the presence of fluorene in phenanthrene has been established by utilizing either the slow rate of carbonation of sodium phenanthrene or the normal carbonation of potassium phenanthrene.

In ethylene glycol dimethyl ether as a solvent, sodium reacts with phenanthrene and upon carbonation sodium salts are obtained. When acidified and purified the product was shown to consist chiefly of *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene (III). Its structure as a 9,10-derivative was established by the fact that it was oxidized by potassium ferricyanide to 9-carboxyphenanthrene (XII), and by chromic acid to phenanthraquinone.

The *trans*-9,10-dicarboxylic acid formed a methyl ester, m. p. 128° (IV). Upon treatment of the acid with acetic anhydride, it formed an anhydride which was converted to a methyl ester, m. p. 119° (VII), not identical with that obtained from the original acid. Since the anhydride made as described would most probably be the *cis* form, it may be deduced that the original acid was the *trans* form. Upon heating the *trans* acid above its melting point in an atmosphere of nitrogen, water but no carbon dioxide was evolved. The product consisted largely of the *cis*-9,10-dicarboxy-9,10-dihydrophenanthrene anhydride (V), with some 9,10-dicarboxyphenanthrene anhydride (VIII).

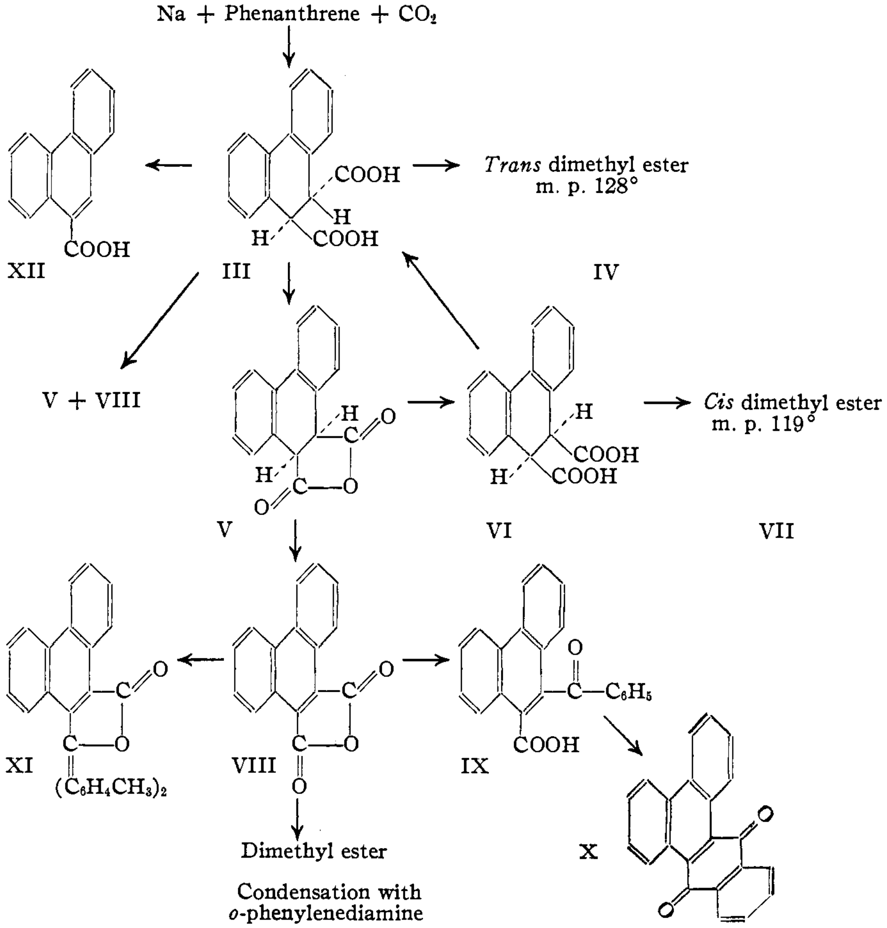
The anhydride obtained from the *trans* acid by treatment with acetic anhydride (V) gave a *cis* acid (VI) when hydrolyzed by dilute alkali in the cold. This *cis* acid was very readily converted into the *trans* form (III) by warming in dilute alkali or by heating with glacial acetic acid. It has never been obtained free from 9,10-dicarboxyphenanthrene anhydride which appears when the solution of the *cis* salt is acidified. Upon melting, the *cis* acid formed the corresponding anhydride and some 9,10-dicarboxyphenanthrene anhydride.

A definitely unstable condition results when the two carboxyls in the 9,10-positions of phenanthrene or of 9,10-dihydrophenanthrene are in the *cis* position. A marked difference exists in the means of escape from this unstable situation shown by the *cis*-dihydro acid and by the dehydro acid. The former shifts into the *trans* configuration or loses hydrogen very readily but loses water only with comparative difficulty; the acid must be heated to melting before dehydration occurs. The dehydro acid has no alternative except to lose water to form its anhydride, which it does spontaneously.

The anhydride of 9,10-dicarboxy-9,10-dihydrophenanthrene (V) could be oxidized quantitatively with chromic acid to the 9,10-dicarboxyphenanthrene anhydride (VIII). This latter product acted in many respects like phthalic anhydride.

It formed by the Friedel and Crafts reaction 9-aroyl-10-phenanthroic acids (IX), which, however, were very difficult to convert to the corresponding substituted anthraquinones. The anthraquinone from the 9-benzoyl-10-phenanthroic acid (X) proved to be identical with that described by Clar[5] made by a different procedure. The anhydride could not be esterified directly with methanol and sulfuric acid, but was converted to the methyl ester by means of alkali and dimethyl sulfate. Neither was it possible to prepare the free 9,10-dibasic acid; only anhydride was recovered. The anhydride condensed readily with *o*-phenylenediamine to the expected cyclic compound. It was also converted to a phthalein (XI).

The various transformations just discussed are given in the chart.



There are several interesting theoretical considerations in connection with the reactions just described: (1) the mechanism of the inversion of the geometrical isomers of the 9,10-dicarboxy-9,10-dihydrophenanthrene; (2) the ease of formation of 9,10-dicarboxyphenanthrene (VIII) from the *cis*-dihydro acid; (3) the ease of formation of the anhydride of 9,10-dicarboxyphenanthrene from the corresponding acid; (4) the mechanism of the addition of sodium to phenanthrene; (5) the role of the solvent, ethylene glycol dimethyl ether.

(1) The *cis*-dihydro acid (VI) is converted into the *trans* form (III) by warming with dilute aqueous alkali or by heating with glacial acetic acid. This conversion may be accomplished through intermediate mono- or dienolized forms shown in XIV and XV.

Evidence of the existence of such intermediates is furnished by the orange color of the *cis* acid in dilute sodium hydroxide solution. The additional conjugation in XIV or especially in XV where an *o*-quinoidal system is present may account for this color. If the solution is warmed, the intensity of the color diminishes until a pale

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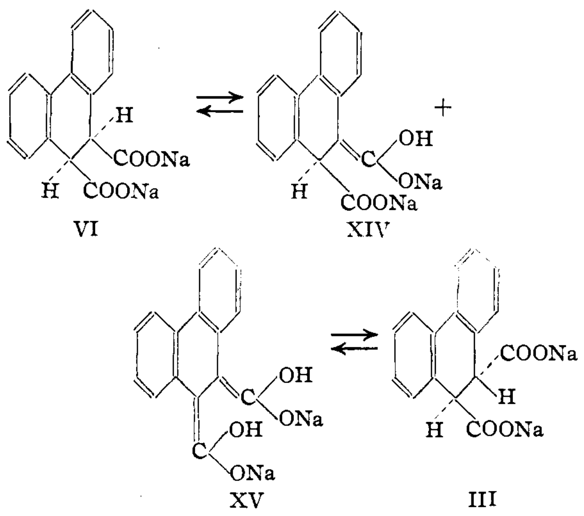
[5] Clar, *Ber.*, **62**, 350 (1929).



VI XIV

XV III

yellow results. From this pale yellow solution only the *trans* acid has been isolated. The pure *trans* acid forms a practically colorless solution in cold or warm 10% aqueous sodium hydroxide. The stability of the *trans* form as compared to the *cis* causes the intermediate enolic forms to rearrange to the *trans* modification rather than to revert to the *cis* form. The light color of the solution of the *trans* acid in aqueous sodium hydroxide indicates the slight tendency of the *trans* acid to enolize as compared with the *cis* acid.

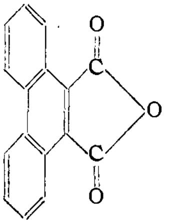
When the *trans*-dihydro acid (III) is heated with acetic anhydride, the product isolated is the *cis*-dihydro anhydride (V). Since this is a dehydration reaction, the possible intermediate *trans* anhydride or its polymer probably shifts through an enol form to the more stable *cis* anhydride configuration. The heat conversion of the *trans* acid to the *cis* anhydride may be explained similarly.

The possibility of enolization of the *cis*-dihydro anhydride is indicated by the fact that when pure in the solid state it is colorless but it gives a yellow solution in acetic anhydride.

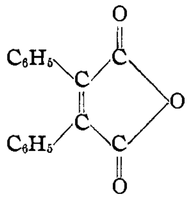
(2) The *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene (III) is not oxidized by means of chromic acid in glacial acetic acid at 100°. On the other hand, the corresponding *cis* acid (VI) in the same solvent but at room temperature is oxidized to 9,10-dicarboxyphenanthrene (VIII) which is isolated as the anhydride. During the isolation of the *cis*-dihydro acid (VI), formed by acidification of a cold solution of the sodium salt, an appreciable amount of the dehydro product, 9,10-dicarboxyphenanthrene anhydride, was formed. The *cis*-dihydro anhydride is oxidized very readily to the dehydrogenated product by means of chromic acid in acetic anhydride. On heating the *trans*-dihydro acid, the anhydride of the *cis* acid forms and is always accompanied by dehydro anhydride. It thus appears that oxidation or dehydrogenation of substituted 9,10-dihydrophenanthrenes takes place readily only when there are two *cis* hydrogens. The conversion of the *trans*-dihydro acid, which has a pair of *trans* hydrogens, into 9-phenanthroic acid (XII) by oxidation with potassium ferricyanide in alkaline solution, takes place only with simultaneous loss of carbon dioxide. This loss of carbon dioxide is not due to the action of the hot alkali. Inversion to the *cis* isomer cannot precede oxidation, for the *trans* form is the stable one in hot alkaline solutions.

(3) The 9,10-dicarboxyphenanthrene anhydride is suprisingly stable. It dissolves only slowly even in hot 10% aqueous alkali. The solution, upon cooling and careful acidification, gives a white precipitate, presumably of the dibasic acid, but before it can be filtered and dried it has reverted to the yellow anhydride. It resisted all attempts at esterification with methanol and sulfuric acid and only by the action of alkali and dimethyl sulfate could this be accomplished.

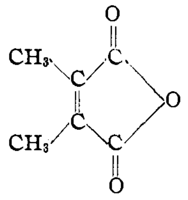
In stability of the anhydride (VIII) and great instability of the acid, this compound resembles diphenylmaleic (XVI) and dimethylmaleic anhydrides (XVII).



VIII



XVI

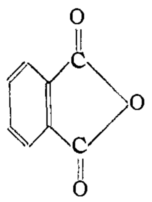


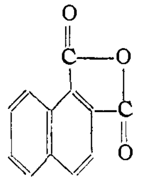
XVII

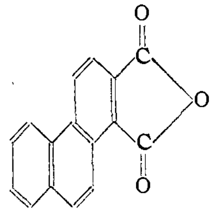
These substances are similar in that the geometrical arrangement of the carboxyl groups is restricted to the *cis* position and the valences of the double-bonded carbon atoms involved in the anhydride group are substituted by groups other than hydrogens.

On the other hand, the following dibasic acids and their anhydrides show various gradations of relative stability.

All three, XVIII, XIX, XX exist in both acid and anhydride forms. The acid of XIX is unstable and forms the anhydride much more readily

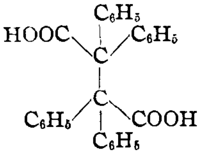

XVIII

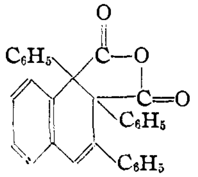

XIX


XX

than the acid of XVIII. The acid of XX is even more unstable and difficult to obtain than that of XIX. Phthalic anhydride XVIII differs from XIX and XX in that an *alpha* substituent is present in the latter two compounds. Moreover, the bonds are not fixed in XVIII, whereas in XIX and XX they are much less mobile and probably exist almost exclusively in the positions shown.

Two other compounds which may be mentioned in connection with this discussion are shown in XXI and XXII. The tetraphenyl succinic compound (XXI) exists both as acid and anhydride.


XXI


XXII

It is different from the other compounds (VIII, XVI–XX) in that the carbon atoms carrying the carboxyl and phenyl groups can rotate about their common bond to a position of maximum stability. The compound 1,2,3-triphenyl-1,2-dicarboxy-1,2-dihydronaphthalene (XXII), however, exists only as an anhydride in contrast to 1,2-dicarboxynaphthalene (XIX) which can exist both as acid and anhydride. With the exception of the two last compounds (XXI and XXII), a common structural feature is present such that each can be thought of as derived from a substituted maleic acid.

The relative immobility of the systems taken alone is not an explanation of the stability of the acids, for although the carboxyl groups in phthalic acid (XVIII) are maintained in the *cis* position, this acid does not spontaneously form an anhydride while acids XVI and XVII also have the carboxyl groups limited to the *cis* position and these do spontaneously lose water to form the cyclic anhydride. The difference in the various acids can be accounted for, however, if, in addition to the effect of the unalterable *cis* configuration of carboxyl groups is added the effect of proximity in space of these carboxyls held in the *cis* position.

This bringing of the carboxyl groups of these dibasic acids so closely together that interaction occurs with varying ease, can be accounted for by the assumption that the presence of the substituents on the maleic acid system so alters the valence angles that the angular divergence between the C—COOH bond and the plane of the C=C bond is decreased below the normal 125.25° angle.

The difference in the spatial effects between 9,10-dicarboxyphenanthrene anhydride (VIII) and the anhydrides of 1,2-dicarboxynaphthalene (XIX) or 1,2-dicarboxyphenanthrene (XX) is probably due principally to the effect of the extra benzene ring and to the presence of two substituents on the carbons holding the carbonyl groups in the first compound, as compared with no extra benzene ring and only one substituent on the carbons holding the anhydride linkage in the last two compounds. There is, however, in addition to the spatial influences of the *alpha* substituents, the possibility of electronic effects. In 9,10-dicarboxyphenanthrene, definite evidence on such effects is furnished by the unusually olefinic nature of the 9,10-carbon–carbon double bond. The high degree of unsaturation of this linkage should be of significance in the stability of the anhydride, for the 9,10-bonds display olefinic properties to an extent not shown by the other double bonds in the phenanthrene ring or, indeed, in naphthalene or benzene. 9,10-Dicarboxyphenanthrene should, therefore, be, as it is, more like diphenylmaleic or dimethylmaleic acid. Comparison of interatomic distances indicates that the greater the unsaturation of a carbon–carbon linkage, the closer the atoms are held together.[6,7] The decrease in interatomic distances would result in the carboxyls involved being brought into closer positions than would be the case in 1,2- or 3,4-dicarboxyphenanthrene.

Fries[8] has explained the high energy states of the double bond at the 9,10-positions in phenanthrene as due to the sharing of the other two double bonds of the central ring with the terminal benzenoid nuclei. Since his theory assumes that in a polynuclear hydrocarbon each ring tends to

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[6] Pauling, Brockway and Beach, THIS JOURNAL, **57**, 2705 (1935).

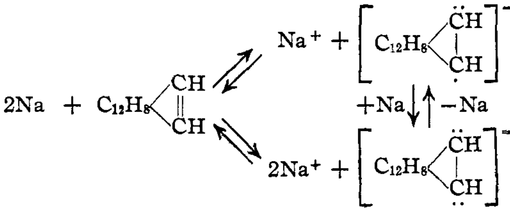
[7] Robertson, *Chem. Rev.*, **16**, 434 (1935).

[8] Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

assume the bond structure which most nearly approaches the condition of an isolated benzene ring, the two terminal rings in phenanthrene are thought by him to lay principal claim to the two double bonds which are common to the terminal and central rings and results in an imperfect conjugation for the 9,10-double bond.

The stability of the anhydride of 9,10-dicarboxyphenanthrene and its relative stability to the other dibasic anhydrides cited can thus be explained as a result of (a) a decrease in the angular divergence between the carboxyl groups due to the spatial effect of alpha-phenyl groups, and (b) of the unsaturated character of the 9,10-double bond which would make the linear distance between the carboxyl groups approach the corresponding distance in an unsaturated dibasic acid like diphenylmaleic acid.

(4) The theory that the addition products of sodium to olefinic linkages are heteropolar compounds has been upheld by Ziegler[3c] and by Wooster.[9] These products have been shown to conduct electricity. The following explanation of the formation and reaction of alkali phenanthrenes is based on these considerations.



XXIII

XXIV

Phenanthrene in solution reacts on the surface of the metal to form the ion XXIV, which may be produced directly from phenanthrene or through the intermediate ion XXIII. The green color developed in the solution is the same whether sodium or potassium is used. It is postulated that this green color is probably due to the ion XXIV, very likely in solvated form.

This mechanism finds support in the experimental observation that during carbonation the green compound is gradually removed from the reaction mixture, and the end of the reaction is marked by its complete disappearance. However, if carbon dioxide is supplied to a green solution of sodium phenanthrene too rapidly, the green color disappears prematurely. If the carbon dioxide is then swept out by nitrogen, the green color gradually builds up again; and when it is sufficiently dense, if carbon dioxide is once more passed in, but at a slower rate than before, the reaction can be carried to normal completion.

The green color of sodium phenanthrene in ethylene glycol dimethyl ether is destroyed quickly by the addition of a relatively small amount of the solvent. By letting the reaction mixture stand, however, under nitrogen, the green color is again developed and the reaction can then be completed normally. This phenomenon may be due to traces of water in the added solvent which destroy the green ion or possibly to a disturbance of the equilibria by sudden dilution.

The proposed mechanism is somewhat similar to that of Ziegler[10] and Koelsch[11] for other sodium addition reactions.

(5) Scott has pointed out that in the addition of sodium to aromatic hydrocarbons a suitable solvent is of great importance in promoting the reaction. He established the fact that the amount of oxygen in the molecule of the solvent is a factor and showed by experiment that aliphatic mono ethers containing a methoxyl group and having a ratio of oxygen to carbon of not less than 1:4 are capable of promoting these reactions. The fully alkylated glycols and polyhydric alcohols were particularly effective. He has shown, moreover, that in the case of sodium naphthalene the presence of a solvent such as ethylene glycol dimethyl ether is actually necessary for existence of the addition compounds, for complete removal of the solvent causes the addition product to decompose. It would appear then that since the O to C ratio in oxygen solvents for promotion of the formation of these alkali metal compounds has definite limits; the effect of these solvents must depend upon some interaction between the solvents and the reactants or their products.

The specific role of the ethylene glycol dimethyl ether in promoting the alkali addition to phenanthrene seems to be due to a number of factors. It may act merely as any other ionizing solvent to permit dissociation; it may stabilize the ionic products of the reaction through solvation; it may activate the sodium. The donor activity of the oxygens of the solvent might yield such a chelate ion as represented in XXV and thus stabilize the ions present in solution.

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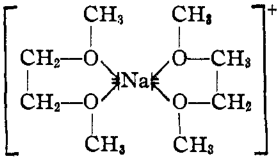
(9) Wooster, *Chem. Rev.*, **11**, 23 (1932).

(10) Ziegler, Colonius and Schäfer, *Ann.*, **473**, 36 (1929).

(11) Koelsch, THIS JOURNAL, **56**, 480 (1934).



XXV

Evidence for the formation of solvated ions like XXV is not lacking. It has been observed that when the addition reaction is well under way, the mixture becomes thick and as the reaction approaches completion the mixture thins out somewhat. This effect was especially noticeable in the reactions where potassium was utilized. The thick mixture became thinner just as the last trace of dark-colored addition product was changed into potassium salts. The solvent had been bound up in some manner and later released.

The solvent is not entirely freed from its combination when the carboxylic salts are formed in the solution. A considerable amount of solvent must remain combined with the salts for relatively little solvent is recovered. Ethylene glycol dimethyl ether boils at 85° and experiment has shown that very little evaporates during the course of a reaction run at 0°. Nor is it likely that decomposition of the ethylene glycol dimethyl ether by sodium or sodium phenanthrene to methyl vinyl ether could account for this disappearance. It appears, therefore, that the carbonated salts are also solvated.

Experimental

Purification of Phenanthrene

In this investigation four different samples of phenanthrene have been employed. The origin and preparation of each of these follow.

Sample I Phenanthrene.—This material was supplied by Scott and Walker of the R. and H. Division of the du Pont Company. It was prepared from the 90% phenanthrene of the Reilly Tar and Chemical Corporation. Four hundred grams of the technical material was agitated for one hour at 150–160° with 25 g. of sodium. On distilling the resultant mixture a 316-g. fraction of phenanthrene was taken leaving a considerable amount of sludge and some phenanthrene in the still. The distillate was agitated with 10 g. of sodium for one-half hour and distilled again, a fraction of 275 g. being taken which was agitated for one hour with 5 g. of sodium before the final distillation. The product, after crystallization from 95% ethanol, was yellowish in color and not free from odor. It started to fuse slightly at 90° and melted completely at 98°. It proved to be completely free from fluorene.

Sample II Phenanthrene.—The phenanthrene used for most of the experiments in this investigation was obtained from the 90% phenanthrene of the Reilly Tar and Chemical Corporation by Bachmann's method of purification.[12] This consists of oxidizing the hydrocarbon by chromic acid in glacial acetic acid solution, distilling the product, and crystallizing from alcohol. The product obtained formed large, firm plates, slightly yellowish, melting at 98–99.5°. Fluorene was shown to be present in this material by a modification of the method of Anschütz.[13] For this purpose a portion of the purified hydrocarbon was oxidized by excess chromic acid in glacial acetic acid solution to 9,10-phenanthraquinone and 9-fluorenone. Steam distillation of the oxidation product removed any unreacted hydrocarbon and some fluorenone. By dissolving the yellow distillation product in 75% methanol and permitting slow evaporation of the solvent, crystals characteristic of fluorenone were obtained.

A fluorene content of about 10% was shown to be present in this sample of phenanthrene by the slow carbonation of its sodium addition product and by the carbonation of its addition product with potassium.

Sample III Phenanthrene.—The "Pure Phenanthrene" of the Gesellschaft für Teerverwertung (Druisberg–Meiderich) was used; the method of purification is unknown to us. It was colorless and odorless and melted from 98–101°. It was found to contain about 1.5% of fluorene.

Sample IV Phenanthrene.—This was synthetic phenanthrene, kindly furnished us by Dr. Perlman[14] of the College of The City of New York.

***trans*-9,10-Dicarboxy-9,10-dihydrophenanthrene (III). From Fluorene-free Phenanthrene (Sample I).**—A solution of 50 g. of this phenanthrene in 250 cc. of ethylene glycol dimethyl ether was prepared in a 1-liter, three-necked flask provided with a mechanical stirrer. One neck of the flask was fitted with a stopper carrying a short piece of large glass tubing closed with a cork which had a hole of small bore through it. The solution was cooled by placing the flask in crushed ice, and dry nitrogen passed through the flask to remove the air. Thin strips of sodium, totaling in weight 17 g., were added. Even though care was taken to add oxide-free sodium, it was generally necessary to cut some of the pieces of sodium in the reaction mixture in order to get a perfectly clean surface to aid in starting the reaction. A dark green, mossy precipitate formed at once on these freshly exposed surfaces, and then spread entirely over each piece of metal. The stirrer was started. A pale green color appeared in the solution and changed rapidly to a dense green. Then dark green, insoluble particles became apparent in rapidly increasing amount. At this stage the nitrogen stream was replaced by one of dry carbon dioxide, which was regulated to a slow stream of bubbles of gas (80–90 cc. per minute) and was passed over the surface of the reaction mixture. In a short time the mixture appeared brown, due to suspended particles, but the solution was still green. At the end of one to one and a half hours, the reaction mixture had become thick with this very dark brown or black suspension, and yellow-colored sodium salts gradually formed on the surface of the mixture. In two and a half hours the dark color had been replaced entirely by the yellow color of the insoluble so-

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(12) W. E. Bachmann, THIS JOURNAL, **57**, 557 (1935).

(13) Anschütz, *Ber.*, **11**, 1216 (1878).

(14) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1936).

dium salts, and the mixture had become somewhat thinner. This marked the end of the reaction.

The mass of unused sodium, coated with a jet-black deposit, was removed by forceps and the thick, solid product was poured and scraped from the flask. No appreciable amount of solvent was left; that remaining was allowed to evaporate spontaneously. When dry, the product weighed 113 g. It was pulverized and extracted for one to two hours with 100 cc. of water at room temperature. The water insoluble material was washed twice with a little water and the washings added to the original filtrate. About 21 g. of water insoluble material was obtained. Dilute hydrochloric acid was added slowly, with stirring, to the brown-colored aqueous solution. Carbon dioxide was liberated, and a tar formed before the solution was acid to litmus. By sufficient care this tar can be precipitated and removed from the solution before any crystalline acids are deposited. The acidification was carried past a congo red end-point and the cream-colored acid completely precipitated; yield, when dry, 24 g. (31% based on phenanthrene).

For purification, the product was extracted twice with boiling chloroform which dissolved the remaining tarry material and left the white insoluble *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene. The latter was crystallized from glacial acetic acid, forming hard, white, rectangular crystals, m. p. 235–242°, with decomposition. The melting point varies somewhat and is usually no sharper than that indicated. The product may also be crystallized from 75% ethanol. It is insoluble in chloroform, benzene and petroleum ether.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.47. Found: C, 71.80; H, 4.57.

The amount of sodium that reacts varies roughly between 35 and 70%. The yield of acid, however, does not run parallel to the sodium consumed.

Only by so regulating the conditions that the sodium does not form a lump some ten to twenty minutes after the reaction has started, can a better yield of product be expected. The mixture is stirred rapidly at first and more slowly as it becomes thicker.

The result of introducing the carbon dioxide more slowly will be described in the latter part of this experimental section.

From Phenanthrene Containing Fluorene (Sample II).—This reaction was conducted exactly as has just been described. The results differed from those of the preceding reaction only in the colors displayed by the reaction mixture and by the presence of 9-fluorenecarboxylic acid in the product obtained. There was no difference in rate of reaction or yield in these two experiments.

A dark brown or black powdery covering formed on the freshly exposed surfaces of the sodium metal in the solution of the phenanthrene in ethylene glycol dimethyl ether. The light red color that first appeared in the solution soon changed to pale brown, this to dense brown, and finally an intense green color prevailed. After the carbonation had continued for some time, the mixture became thick with suspended brown particles, and soon thereafter orange-colored sodium salts appeared. At the end of the reaction the mixture was a thick mass, bright orange in color; reaction time, 2.5 hours, using 50 g. of phenanthrene. The product became tan and then brown as it dried.

The product was worked up just as described before. Under the conditions of this experiment the amount of 9-fluorenecarboxylic acid formed was not large. Some of it was precipitated along with the tarry by-product before the aqueous solution was acid to congo red. The remainder of it was allowed to precipitate along with the main reaction product. Extraction of this mixture with a small amount of boiling chloroform removed most of the remaining tar present, a couple of further extractions of the residue with large volumes of boiling chloroform dissolved the 9-fluorenecarboxylic acid and left the *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene quite pure.

A more detailed discussion of the separation and purification of 9-fluorenecarboxylic acid is given under the description of the slow carbonation of sodium phenanthrene and in the discussion of the acid itself.

From Phenanthrene Containing Fluorene (Sample III).—This phenanthrene was treated in the same way as has been described for Samples I and II. The coating that formed on the sodium as the reaction was beginning was dark green in color. The entire solution became green in about ten minutes time, without formation of intermediate colors. After fifteen minutes of reaction time, dark green insoluble particles were floating in the solution. As carbonation progressed the mixture became brown and finally dingy yellow in color. The product was worked up as described before.

From Synthetic Phenanthrene (Sample IV).—A 5-g. portion of this was used in the usual way. The surface of the sodium became coated with a dark deposit (brown or green?), the solution soon became pale green and then dense green without intermediate colors. During carbonation the mixture became brown, and finally orange-colored when the reaction was complete. Total reaction time, one hour. The product was worked up in the usual way.

***trans*-9,10-Dicarbomethoxy-9,10-dihydrophenanthrene (IV).**—Pure *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene was esterified with absolute methanol and a few drops of concentrated sulfuric acid. The ester crystallized from the cold reaction mixture and was purified by recrystallization from methanol. It formed white shining plates, m. p. 128°, yield quantitative.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 72.98; H, 5.40.

9-Phenanthroic Acid (XII) from *trans*-9,10-Dicarboxy-9,10-dihydrophenanthrene.—To a solution of 1 g. of *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene in aqueous potassium hydroxide (1.5 g. of potassium hydroxide in 8 cc. of water) was added 2.64 g. of potassium ferricyanide in 8 cc. of water. After heating the mixture on a steam-bath for two and one-half hours, a yellowish sediment was removed and the filtrate acidified with dilute hydrochloric acid. The bluish precipitate was filtered, washed, and recrystallized twice from methanol and then twice from benzene. White needles, m. p. 252°, were thus obtained; yield 0.2 g. The melting point is the same as that reported by Mosettig,[15] and by Bachmann.[16]

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[15] Mosettig, THIS JOURNAL, **54**, 3328 (1932).

[16] Bachmann, *ibid.*, **56**, 1363 (1934).

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 81.08; H, 4.50. Found: C, 80.71; H, 4.59.

The methyl ester prepared from methanol and a few drops of sulfuric acid had a melting point of 115° which agrees with that found by Schoppee[17] for methyl-9-phenanthroate.

Heat Decomposition of *trans*-9,10-Dicarboxy-9,10-dihydrophenanthrene (III).—Pure *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene was heated in an atmosphere of nitrogen in a flask immersed in an oil-bath at 220°. As the bath temperature was raised to 260° the solid melted with vigorous evolution of gas which continued for about three minutes. During the reaction water but no carbon dioxide was eliminated.

After cooling, the solid product was pulverized and treated for an hour with 10% aqueous sodium hydroxide at room temperature. Much of it dissolved, giving an orange-colored solution. The insoluble material was removed.

(a) Portion Soluble in Cold Dilute Aqueous Sodium Hydroxide.—Upon acidification of the alkaline solution a fine white precipitate formed which became yellow when filtered and dried. This crude acid fused at 196°, solidified and then melted completely at 235–240°. These are characteristic properties of *cis*-9,10-dicarboxy-9,10-dihydrophenanthrene. The crude acid was esterified with methanol and a few drops of concentrated sulfuric acid. Some insoluble yellow material did not dissolve and was removed. This insoluble material was purified by recrystallization from acetic anhydride and formed yellow rod-like crystals, m. p. 322°. It proved to be 9,10-dicarboxyphenanthrene anhydride which will be described in more detail later.

The methyl alcoholic solution after removal of the yellow insoluble material was allowed to cool and concentrate slowly. Large, flat, pale yellow needles formed, which after recrystallization from methanol were almost colorless and melted at 119°. This proved to be identical with *cis*-9,10-dicarbomethoxy-9,10-dihydrophenanthrene to be described later.

(b) Portion Soluble in Hot Dilute Aqueous Sodium Hydroxide.—The residual material from the cold aqueous sodium hydroxide extraction dissolved completely when heated for some time with 10% aqueous sodium hydroxide. The colorless solution was acidified; a white precipitate formed which became increasingly yellow on standing, filtering and drying. The crude substance melted at 308°. Crystallization from acetic anhydride produced small yellow rods, m. p. 322°. This was 9,10-dicarboxyphenanthrene anhydride.

Oxidation of *trans*- and *cis*-9,10-Dicarboxy-9,10-dihydrophenanthrene (III) and (VI) with Chromic Acid.—To a solution of 1.34 g. of *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene in 10 cc. of hot glacial acetic acid that had cooled somewhat, was added slowly with stirring 1.5 g. of chromic anhydride in 10 cc. of glacial acetic acid. After the initial vigorous reaction, the mixture was heated on a steam-bath for thirty minutes. The solution was cooled and poured into ice and water. The precipitate was filtered, washed with sodium bicarbonate solution and dissolved in a saturated solution of sodium bisulfite. After filtration and acidification of the filtrate, the orange product was removed and purified by crystallization from 75% alcohol, m. p. 207.5–208.5°. It proved to be 9,10-phenanthraquinone.

To a solution of 0.50 g. of *cis*-9,10-dicarboxy-9,10-dihydrophenanthrene in 5 cc. of cold glacial acetic acid was added slowly with stirring 0.15 g. of chromic anhydride in 5 cc. of cold glacial acetic acid. Reaction began at once; after thirty minutes the solution was green and a yellow precipitate had separated. After two hours precipitation was complete. The insoluble material was removed, washed on the filter with water, treated with warm 5% sulfuric acid, washed and dried. The yellow product was crystallized from acetic anhydride, m. p. 322°. A quantitative conversion to 9,10-dicarboxyphenanthrene anhydride had been made.

9,10-Dicarboxy-9,10-dihydrophenanthrene Anhydride (V).—A solution of 5 g. of pure *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene in 10 cc. of acetic anhydride was heated under reflux for two hours. It was allowed to cool slowly for several hours and then chilled with ice. One crystallization from acetic anhydride gave a pure product, dull yellow rods, m. p. 193.5°; yield, 4.22 g. (90%).

A sample of this anhydride after sublimation was colorless, m. p. 193.5°. Crystallization from acetic anhydride produced a pale yellow product, probably due to the presence of traces of 9,10-dicarboxyphenanthrene anhydride.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.80; H, 4.00. Found: C, 76.54; H, 4.10.

The filtrates from the preparation and recrystallization of the above anhydride were allowed to stand in a closed container for some time. A finely divided precipitate gradually settled out. It melted at 322° after recrystallization from acetic anhydride and proved to be 9,10-dicarboxyphenanthrene anhydride (VIII).

Hydrolysis of 9,10-Dicarboxy-9,10-dihydrophenanthrene Anhydride to the *cis*-Dihydro Acid (VI).—A solution of pure 9,10-dicarboxy-9,10-dihydrophenanthrene anhydride in 20 cc. of 10% aqueous sodium hydroxide was prepared by standing at room temperature for an hour with occasional stirring. The solution was orange-colored. Some fine yellow precipitate formed, but dissolved when the solution was diluted to twice its volume with cold water. This precipitate was the sodium salt of the *cis*-dihydro acid. The diluted solution was freed from a small amount of orange-colored insoluble material of undetermined nature, and carefully acidified with 3 *N* hydrochloric acid. The fine white precipitate first formed soon became yellow. A yield of 2.9 g. of dry acid resulted, which fused and lost water at 196°, solidified, and melted completely at 232° without decomposition. This acid was *cis*-9,10-dicarboxy-9,10-dihydrophenanthrene.

The product was divided into three portions and treated separately as follows:

(a) Crystallization from Glacial Acetic Acid.—The *cis* acid is more soluble in glacial acetic acid than is the corresponding *trans* form. A small amount of insoluble 9,10-dicarboxyphenanthrene anhydride was removed from the hot solution. After cooling, the crystalline product obtained melted at 235–243° with vigorous decomposition. It was the *trans*-dihydro acid. No other material was obtained from this solution.

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[17] Schoppee, *J. Chem. Soc.*, 40 (1933).

(b) Esterification.—The second portion of the crude *cis* acid was esterified in the usual way with methanol and a few drops of concentrated sulfuric acid. A small amount of yellow insoluble material was removed from the hot solution; it proved to be 9,10-dicarboxyphenanthrene anhydride. By allowing the alcoholic filtrate to cool and concentrate slowly, large yellowish needles formed. Recrystallization from methanol produced pale yellow needles, m. p. 119°. The entire product consisted of *cis*-9,10-dicarbomethoxy-9,10-dihydrophenanthrene (VII).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 72.31; H, 5.00.

(c) Treatment with Warm Aqueous Sodium Hydroxide Solution.—The third portion of the crude *cis* acid preparation was dissolved in cold 10% aqueous sodium hydroxide and a small amount of insoluble 9,10-dicarboxyphenanthrene anhydride removed. The orange-colored filtrate was warmed on the steam-bath for fifteen minutes. The color gradually became yellow. When cooled, the solution remained free from precipitate. Acidification produced a slightly gummy white precipitate which did not become yellow. When dry, this melted with vigorous decomposition at 240–245°. The acid was esterified without further treatment. From the cooling alcoholic solution iridescent plates separated, which after recrystallization from methanol melted at 128°. This was *trans*-9,10-dicarbomethoxy-9,10-dihydrophenanthrene. No trace of the corresponding *cis* ester was found.

When the pure 9,10-dicarboxy-9,10-dihydrophenanthrene anhydride was dissolved by warming for fifteen minutes in 10% aqueous sodium hydroxide, the original orange-colored solution became pale yellow and acidification of the cold solution produced a white precipitate. This product was *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene.

Heat Decomposition of *cis*-9,10-Dicarboxy-9,10-dihydrophenanthrene.—A small amount of the *cis* acid prepared as described above was placed in a small flask and the air replaced by nitrogen. The flask was immersed in an oil-bath at 160°. At 200° fusion occurred with liberation of water and immediate resolidification. At 230–240° the substance melted completely without decomposition and was removed from the bath at once. After cooling, the yellow melt was pulverized and esterified without further treatment. The solid dissolved slowly, with the exception of a small amount that remained undissolved and was removed. This was found to be 9,10-dicarboxyphenanthrene anhydride. From the alcoholic solution the crystals characteristic of *cis*-9,10-dicarbomethoxy-9,10-dihydrophenanthrene separated. It was the only product obtained.

9,10-Dicarboxyphenanthrene Anhydride (VIII).—To a solution of 2.5 g. of 9,10-dicarboxy-9,10-dihydrophenanthrene anhydride in 10 cc. of boiling acetic anhydride that had been cooled to 80° was added slowly with stirring 1.3 g. of chromic anhydride in 10 cc. of acetic anhydride. The reaction mixture was kept on a steam-bath. An exothermic reaction occurred and a yellow precipitate began to settle out. After fifteen minutes, it was allowed to stand for four hours and then cooled in ice. The orange solid was isolated, dried, and purified by crystallization from 155 cc. of acetic anhydride. It formed yellow rod-shaped crystals, m. p. 322°; yield 2.3 g. (92%). It may be crystallized from dioxane but is only very slightly soluble in the other common solvents.

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.44; H, 3.21. Found: C, 77.39; H, 3.07.

This anhydride can be dissolved completely only by boiling in hot alkali. If a solution of the anhydride in warm alkali is cooled and carefully acidified with dilute hydrochloric acid, a white precipitate, presumably of acid, separates but this turns yellow on filtering and by the time it is dry it is completely yellow and is essentially pure anhydride.

9,10-Dicarbomethoxyphenanthrene.—It was found impossible to convert 9,10-dicarboxyphenanthrene anhydride to the dimethyl ester by means of methanol and sulfuric acid. After long heating most of the anhydride dissolves but is recovered from solution unchanged.

A solution of 3.5 g. of potassium hydroxide in 10 cc. of water, 5 cc. of methanol and 0.5 g. of 9,10-dicarboxyphenanthrene anhydride was heated on the steam-bath for one hour. About 8 cc. of dimethyl sulfate was added gradually with stirring and from time to time dilute methyl alcoholic potassium hydroxide to keep the solution basic. Upon cooling, yellow crystals separated which were purified from 95% ethanol. It formed pale yellow rectangular plates, m. p. 131°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.49; H, 4.76. Found: C, 73.39; H, 5.00.

9-Benzoyl-10-phenanthroic Acid (IX).—To a well-cooled solution of 10 g. of 9,10-dicarboxyphenanthrene anhydride in 40 cc. of dry benzene, was added 11 g. of powdered anhydrous aluminum chloride with stirring. The reaction mixture was warmed during one hour until the temperature was 90°. The color changed from bright orange to brown and then to green. After three hours at this temperature the mixture was cooled, ice and 15 cc. of concentrated hydrochloric acid were added. After removal of the benzene by steam distillation, the residual material was dissolved in hot 5% aqueous sodium carbonate, the solution filtered from about 2.5 g. of unreacted anhydride, and then acidified. The precipitate was removed, dried and purified by two crystallizations from a large volume of boiling chloroform. The product thus formed contains chloroform of crystallization. On drying *in vacuo* at 100°, a white powder is obtained, m. p. 232°; yield 9 g. (92%).

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.79; H, 4.28. Found: C, 80.70; H, 4.30.

9-(*p*)-Toluyl-10-phenanthroic Acid and Ditolylphenanthphthalein (XI).—A mixture of 1.25 g. of 9,10-dicarboxyphenanthrene anhydride, 7 cc. of dry toluene and 1.5 g. of anhydrous aluminum chloride was allowed to react as described in the previous preparation. The total reaction time was two and one-quarter hours. The solid residue, after steam distillation of the toluene, was extracted with hot 5% aqueous sodium carbonate solution. The insoluble material was removed and the solution acidified. The precipitate was purified by crystallization from toluene. It was obtained as light buff-colored crystals fusing slightly at 231° and melting at 236°. The substance gave a deep green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.17; H, 4.70. Found: C, 81.20; H, 4.70.

The sodium carbonate insoluble material was also insoluble in aqueous sodium hydroxide. It was purified by recrystallization from glacial acetic acid: white plates, m. p. 247°. It proved to be a phthalein. It gave no color with concentrated sulfuric acid.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.95; H, 5.31. Found: C, 87.07; H, 5.53.

1,2,3,4-Dibenzanthraquinone (X).—A thorough mixture of 9-benzoyl-10-phenanthroic acid and excess phosphorus pentoxide was immersed in a bath at 220° and the temperature was raised to 260° in about five minutes' time, pressing the mixture together during the heating. After cooling somewhat, hot water was added, and the solid was removed and treated with dilute aqueous ammonia. The residue was extracted with 75% alcohol which dissolves the quinone. The quinone separates on cooling and more is obtained by evaporation of part of the alcohol. The product was purified from glacial acetic acid, m. p. 181–183°, yield 10–15%. Clar[5] gives a melting point of 179°.

Anal. Calcd. for $C_{22}H_{12}O_2$: C, 85.71; H, 3.89. Found: C, 85.25; H, 4.00.

Reaction of Benzoyl Chloride on 9-Benzoyl-10-phenanthroic Acid.—A recent patent[18] describes the reaction of aroyl benzoic acids and benzoyl chloride in trichlorobenzene to give anthraquinones. With 9-benzoyl-10-phenanthroic acid, however, this procedure gave not the anthraquinone but merely the ketolactone of the original product.

A mixture of 1 g. of 9-benzoyl-10-phenanthroic acid, 3 cc. of benzoyl chloride and 6 cc. of trichlorobenzene was heated under reflux for three hours. After standing several hours, white crystals separated and after filtration and partial evaporation of the filtrate a further crop was obtained. This proved to be unchanged starting material. Upon complete evaporation, a tar was left which was extracted with glacial acetic acid. On cooling, yellow crystals formed which, after further purification from glacial acetic acid, had a melting point of 228° and proved to be the ketolactone.

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.79; H, 4.28. Found: C, 81.50; H, 4.21.

Upon treatment of this compound with hot alcoholic potassium hydroxide, solution took place and upon acidification 9-benzoyl-10-phenanthroic acid resulted.

Reaction of 9,10-Dicarboxyphenanthrene Anhydride with *o*-Phenylenediamine.—A mixture of 0.25 g. of 9,10-dicarboxyphenanthrene anhydride and 0.15 g. of *o*-phenylenediamine was pulverized and heated in an oil-bath at 140°. In the course of twenty-five minutes the temperature was raised to 300° and then the flask was heated with a free flame until the molten mass became red. The product was pulverized and dissolved in acetic anhydride. After one recrystallization it was pure and formed deep orange needles, m. p. 279°. It gave a crimson color with sulfuric acid.

Anal. Calcd. for $C_{22}H_{12}ON_2$: C, 82.50; H, 3.75; N, 8.75. Found: C, 82.69; H, 4.00; N, 8.86.

Reaction of 9,10-Dicarboxy-9,10-dihydrophenanthrene Anhydride with *o*-Phenylenediamine.—A mixture of 0.25 g. of anhydride and 0.15 g. of *o*-phenylenediamine was pulverized and heated to 100°. The temperature was raised and fusion was complete at 135°. At 145° the melt began to form a yellow solid. After twelve minutes at 200°, the heating was stopped. By extraction with glacial acetic acid, much remained undissolved. From the solution, yellow-orange crystals separated, m. p. 274°. The compound gave a yellowish-pink color with concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{14}ON_2$: C, 81.98; H, 4.35. Found: C, 82.36; H, 4.65.

Slow Addition of Carbon Dioxide to Sodium Phenanthrene.—A solution of 100 g. of phenanthrene (containing fluorene, sample II) in 500 cc. of ethylene glycol dimethyl ether was treated with 35 g. of sodium as previously described. The mixture was stirred for fifteen minutes, after ten of which it had become dense green. Carbon dioxide was now passed in at about one-third the rate previously described (20–30 cc. per minute). The reaction continued similarly with two exceptions: (1) the sodium salts instead of being uniformly orange contained patches of white; (2) four hours instead of two and one-half hours were required to discharge completely the green color. The 187 g. of sodium salts obtained was added to 150 cc. of water and allowed to stand for several hours with occasional stirring. About 47 g. of water insoluble material was removed and stirred with 50 cc. of water. The filtrates were combined and dilute hydrochloric acid added slowly. At first carbon dioxide was evolved, and tar which formed was removed. Then, when the solution was acid to litmus but not to congo red, a pale-colored precipitate began forming, whereas in experiments in which the normal rate of carbonation had been employed no precipitate was obtained at this point. The precipitate was removed and found to consist entirely of 9-fluorenecarboxylic acid; weight of crude product, 14 g.

The main filtrate was further acidified until precipitation of the *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene was complete; yield 36 g. It was purified as previously described and had a melting point of 235–242°.

The acidified filtrate from the second fraction was allowed to concentrate slowly at room temperature. Fine white crystal clusters separated and were removed and recrystallized from chloroform. The aqueous filtrate was extracted with ether to remove some tarry matter present, concentrated to about one-half and more white crystals obtained. These were extracted by ether to remove tar, and recrystallized from chloroform. The total product (about 1 g.) was white and granular, m. p. 153.5° without decomposition. The substance gave a neutral equivalent of 133. Its identity has not been established.

This same procedure of slow carbonation has been followed utilizing phenanthrene of samples I, III and IV. In each case the description of the reaction is essentially the same as that already given for these samples under the discussion of carbonation at the normal rate. The rate of carbonation was so regulated, however, that from four to five hours was required to complete a reaction. No trace of 9-fluorenecarboxylic acid was obtained from samples I and IV. From sample III the amount of this acid isolated indicated a fluorene impurity of about 1.5%.

9-Fluorenecarboxylic Acid.—The crude 9-fluorenecarboxylic acid obtained above was contaminated with a small

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[18] German Patent, 590,579; *Friedländer*, **20** (II), 1293 (1935).

amount of tarry material. This was removed by treatment with a small volume of warm chloroform which dissolved the tar. The fluorenecarboxylic acid was left colorless and little of it was dissolved. This was then crystallized twice from large volumes of boiling chloroform. White, silky needles, m. p. 224° with slight decomposition resulted. This acid crystallizes well from 75% ethanol, forming long needles in wedge-shaped formations, m. p. 226°. Several months later the melting point of this same material was 232°, with slight decomposition. In some other cases the acid melted at 232° after one crystallization from the crude form. This difference of melting point is dependent somewhat upon rate of crystallization. Crystals that form slowly and without disturbance give the higher melting point and are harder and brighter in appearance than the lower melting form. This double melting point, also reported by those who have previously prepared this substance,[19] is probably due to dimorphism.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76; neut. equiv., 210; mol. wt., 210. Found: C, 79.81; H, 4.84; neut. equiv., 212; mol. wt. (Rast), 223.

This acid corresponds to that obtained by Schlenk,[2] who reported a melting point of 226°, and by Ziegler,[3a] who reported a melting point of 223–224°, and which was believed by them to be 10,10'-dicarboxy-9,9',10,10'-tetrahydro-9,9'-biphenanthryl.

In carbonation reactions of alkali phenanthrenes in which only a small amount of this acid was produced, it was found best to isolate the 9-fluorenecarboxylic acid along with the *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene instead of fractionally precipitating these from the solution of the salts. From the mixture of acids thus obtained the fluorenecarboxylic acid can be completely separated by extraction with large volumes of boiling chloroform.

When the amount of the fluorenecarboxylic acid produced by an alkali metal–carbon dioxide reaction is very small, much of it is separated from the aqueous acidified solution along with the tarry by-product. The fluorenecarboxylic acid can be isolated from this by dissolving the tarry mass in ethyl ether and then slowly concentrating. The fluorenecarboxylic acid crystallizes from the solution and is then washed on the filter with cold 75% ethanol. Several crystallizations from 75% ethanol produce a pure product.

9-Carbomethoxyfluorene.—By heating the acid with methanol and a few drops of concentrated sulfuric acid, the ester was obtained. From absolute methanol, it formed fine, white needles, m. p. 67–68°.

The ester prepared by Schlenk and Bergmann[19a] from 9-fluorenecarboxylic acid melted at 63°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.35; H, 5.35; mol. wt., 224. Found: C, 80.47; H, 5.32; mol. wt. (cryoscopic), 214.

Formation of Fluorene and Fluorenone from 9-Fluorenecarboxylic Acid.—The acid described above, m. p. 232°, dissolved in cold 5% aqueous sodium hydroxide to give a colorless solution. Warmed in the air, under reflux, the solution became yellow and turbid at once. Boiling the solution gently for an hour did not change its aspect, but a white solid collected in the condenser, having been volatilized with steam. This solid was purified from 95% ethanol, giving white flakes, m. p. 115°, and having a characteristic odor resembling coal tar products. This is fluorene.

Anal. Calcd. for $C_{13}H_{10}$: C, 93.98; H, 6.02. Found: C, 93.77; H, 5.83.

When the alkaline solution from above was allowed to stand at room temperature in contact with the air for several hours, the surface of the solution became covered with well-formed, yellow needles. These formed long, yellow needles from 75% methanol and melted at 85°. They gave a violet color with concentrated sulfuric acid. This substance is fluorenone.

Anal. Calcd. for $C_{13}H_8O$: C, 86.66; H, 4.44. Found: C, 86.37; H, 4.24.

The oxime was obtained as yellow crystals from aqueous ethanol, m. p. 194°. The accepted value is 195°.

Fluorenone was also obtained by oxidation of 9-fluorenecarboxylic acid in glacial acetic acid solution by an equal weight of chromic anhydride at room temperature.

Wislicenus and Ruthing[19d] found that 9-fluorenecarboxylic acid forms mostly fluorene if warmed in alkaline solution, while exposure to the air at room temperature results in a fairly rapid and complete conversion to fluorenone.

The Reaction of Phenanthrene with Potassium and Carbon Dioxide in Ethylene Glycol Dimethyl Ether

Phenanthrene, Fluorene-free, Sample I.—The quantities of materials used were in exact proportion to those used in reactions with sodium, and the reaction was conducted in the same way as previously described for sodium. Twenty grams of phenanthrene (Sample I) was dissolved in 100 cc. of ethylene glycol dimethyl ether, cooled to 0°, and the air replaced by dry nitrogen. Twelve grams of clean potassium in small pieces was added, and the stirrer started. A pale red color developed immediately which became red-brown; three minutes after addition of the metal the solution was a dense green; after five minutes dry carbon dioxide was introduced into the flask. After fifteen minutes the mixture was thick with suspended green solid and the unreacted potassium was in a lump After a total reaction time of sixty-five minutes the mixture was considerably thinner and was entirely yellowish-orange in color. During about half of the reaction time the carbon dioxide was passing through the drying agent so that the bubbles of the gas formed a continuous stream with mild splashing of the surface (about 125 cc. per minute). During the other half of the reaction time a stream of about 90 cc. per minute was used. The product was worked up in the usual way, 6 g. of unreacted metal and 8 g. of water-insoluble material was recovered. The red-brown aqueous extract was acidified slowly with dilute hydrochloric acid. Some tar formed and was removed, carbon dioxide was evolved as usual. The first crystalline material precipitated when the solution was acid to congo red. This fraction was removed, and then acidification of the filtrate continued until precipitation was complete; total yield, 8 g. Each of the fractions taken was extracted twice with large volumes of chloroform. No trace of 9-

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(19) (a) Schlenk and Bergmann, *Ann.*, **463**, 188, 192 (1928); (b) Bergmann, *Ber.*, **63**, 1630 (1930); (c) Kliegel, *ibid.*, **64B**, 2420 (1931); (d) Wislicenus and Ruthing, *ibid.*, **46**, 2770 (1913).

fluorenecarboxylic acid was found after concentration of the chloroform filtrates. This result is in agreement with that obtained when the sodium addition product of this sample (I) of phenanthrene was subjected to slow carbonation. The chloroform-insoluble acid was *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene.

Phenanthrene Containing Fluorene (Sample II).—The reaction was conducted as just described. The potassium began to react as soon as it was placed in the solution containing the phenanthrene. The initial red color deepened rapidly and in five minutes after addition of the metal the solution had become dark green in color. Insoluble particles separated from the solution just as they have been described as doing in the sodium reactions, and as has always been observed in reactions with potassium. The mixture became very thick with this suspended matter. At the end of the reaction the product was a bright orange color, reaction time, one hour. The product was worked up as before. After the aqueous extract was acid to litmus, but before the congo red end-point had been reached, a fraction of white solid was removed and found to weigh 3 g. It proved to contain only a little tarry matter and 9-fluorenecarboxylic acid. By acidifying the filtrate from which this fraction had been separated to a congo red end-point, 6 g. of yellowish solid was precipitated, which proved to be *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene. The final aqueous filtrate was extracted with ether and concentrated *in vacuo* at room temperature. About 0.5 g. of white crystalline material was recovered from the concentrated solution and was shown to be the acid of undetermined character melting at 153.5° after crystallization from chloroform. The reaction had gone in exactly the same manner as when sodium phenanthrene solution was carbonated slowly.

Phenanthrene Containing Fluorene (Sample III).—The potassium became coated with a dark deposit as soon as it came in contact with the solution of phenanthrene in ethylene glycol dimethyl ether. A red-orange color developed immediately in the solution. This darkened, became brown and then a dark green, all in about five minutes time. The reaction proceeded as has been described in the two preceding cases. The product was pale gold in color. It was worked up as described for Sample II. 9-Fluorenecarboxylic acid was isolated in the same proportions as it had been when this same sample of phenanthrene had been employed in a slow carbonation reaction, using sodium. This indicated about 1.5% fluorene in the phenanthrene.

Synthetic Phenanthrene (Sample IV).—This gave a pale green color immediately, which rapidly deepened in intensity to give the usual green obtained in these reactions. The reaction product before drying was gold in color. A small amount of the usual tarry material was isolated from the reaction product, the remainder was *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene.

Rapid Carbonation of Potassium Phenanthrene.—The reaction of potassium with phenanthrene (Sample II) was also run in a similar manner as just described, except that the carbon dioxide was passed into the reaction flask at a rate of about 150 cc. per minute throughout the course of the reaction. The metal did not form a lump as it ordinarily does. The reaction was complete in forty-five minutes. A negligible amount of unreacted metal was recovered; 0.2 g. of 9-fluorenecarboxylic acid was obtained from the aqueous extract of the product, and only enough *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene to identify. Apparently the carbon dioxide had combined with the metal and had removed it from the addition product that had been formed.

The Reaction of Phenanthrene with Lithium in Ethylene Glycol Dimethyl Ether.—A reaction tube with two arms identical with the ones utilized by Schlenk in his investigation[20] was prepared and charged as described by this same investigator. Ten grams of phenanthrene (Sample II) 75 cc. of ethylene glycol dimethyl ether and 4 g. of lithium were sealed in the tube under dry nitrogen, and left on the shaking machine at room temperature for twenty-four hours. A crimson colored precipitate appeared in the solution at first but was soon obscured by a dense green color. Without being brought into contact with air, the contents of the tube were added gradually to a large excess of crushed solid carbon dioxide. An exothermic reaction occurred. After spontaneous evaporation of the carbon dioxide and of the solvent, the product was extracted with the smallest amount of water possible and the aqueous extract acidified carefully. A small amount of gas was evolved, and an oily product separated. This oil was dissolved in ether, on slow concentration white crystals separated and were removed from the gummy ether solution. After purification, this solid formed the crystalline structure characteristic of 9-fluorenecarboxylic acid and gave no depression of the melting point when mixed with some of this compound obtained from a potassium preparation. Concentration of the aqueous filtrate from which the oil had been removed produced a small amount of white crystalline material which was insoluble in chloroform, and after crystallization from glacial acetic acid melted at 232–240° with decomposition. It proved to be *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene as determined by general properties and a mixed melting point with an authentic sample. This acid was esterified in the usual way and the product was shown to be the ester of *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene.

When diethyl ether was used in place of ethylene glycol dimethyl ether and the reaction was allowed to run for four days, only 9-fluorenecarboxylic acid was obtained from the water-soluble extract.

Summary

Alkali metals have been added to phenanthrene in ethylene glycol dimethyl ether and the product carbonated. Dependent upon the purity of the phenanthrene used, *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene or this compound with 9-fluorenecarboxylic acid was isolated. This demonstrates that alkali metals add in the 9,10-positions, indicating that Schlenk's interpretation of his results that lithium adds 1,4 to phenanthrene is erroneous.

The proof of the structure of the 9,10-dicar-

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(20) Schlenk and Thal, *Ber.*, **46**, 473 (1913).

boxy-9,10-dihydrophenanthrene was determined by oxidation to 9-phenanthroic acid and to phenanthraquinone.

The acid was shown to be *trans* since upon treatment with acetic anhydride or by heating to fusion, it was converted into an anhydride which on hydrolysis gave a new acid, the *cis* form. The *cis* acid was readily reconverted to the *trans* merely by heating in glacial acetic acid or by warming in sodium hydroxide solution.

The *trans* acid is oxidized with difficulty, the *cis* acid or anhydride with great ease. The latter gives as a product, 9,10-dicarboxyphenanthrene anhydride which shows reactions similar to those of phthalic anhydride.

The identification of 9-fluorenecarboxylic acid is based on the correspondence of its properties with those of a previously described compound of established structure and upon its characteristic conversion into fluorene and fluorenone. The fluorene has been proved to be an impurity present in all natural phenanthrenes that have not been especially treated to remove this impurity.

A theoretical discussion is given of several phases of the work: (1) the mechanism of inversion of the geometrical isomers of the 9,10-dicarboxy-9,10-dihydrophenanthrene; (2) the ease of formation of 9,10-dicarboxyphenanthrene from the *cis*-dihydro acid; (3) the ease of formation of the anhydride of 9,10-dicarboxyphenanthrene from the corresponding acid; (4) the mechanism of the addition of sodium to phenanthrene; (5) the role of the solvent, ethylene glycol dimethyl ether.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Dissociation of Hexa-*p*-alkylphenylethanes[1]

BY MAX F. ROY AND C. S. MARVEL

In a previous paper,[2] the preparation of a series of hexa-*p*-alkylphenylethanes in toluene solution was reported. Also, on the basis of the fact that the depth of color of the ethane solutions increased with the weight of the alkyl group, it was postulated that the dissociation of the ethanes increased as the weight of the alkyl groups increased.

The degrees of dissociation of these hexa-*p*-alkylphenylethanes in one-tenth molar benzene solution at 20° have now been measured by the magnetic method. This method, first suggested by Taylor[3] and more recently elaborated by Müller[4] and his associates, consists in measuring the magnetic susceptibility of a solution of a dissociated hexaarylethane. The molecular susceptibility of the ethane in solution may then be calculated, and a comparison of this observed value with that calculated from Pascal's diamagnetic atomic susceptibilities gives the paramagnetic contribution of that part of ethane which is dissociated. The degree of dissociation of the ethane is then the ratio of this observed paramagnetic contribution to that which might be expected if dissociation were complete.

One-tenth molar solutions of the ethanes were prepared by shaking two-tenths molar benzene solutions of the appropriate tri-*p*-alkylphenylchloromethanes with a large excess of molecular silver. Complete conversion of chloromethane to ethane was assumed in this operation. This assumption is reasonable, because the work of Gomberg and Sullivan[5] has shown that similarly prepared solutions of tetraphenyl-di-β-naphthylethane absorbed 99.6, 102, 102, and 100% of the theoretical amount of oxygen.

The magnetic mass susceptibilities of the ethane solutions were measured by the Quincke hydrostatic method, and the degrees of dissociation were calculated as indicated. The degree of dissociation of hexaphenylethane in one-tenth molar benzene solution at 20° was determined and found to be $2.1 \pm 0.5\%$. This value is in good agreement with the value 2.4% calculated for one-tenth molar solution from the equilibrium constant at 23° found by Müller.[4]

The colors of the solutions and the degrees of dissociation of the hexa-*p*-alkylphenylethanes in one-tenth molar benzene solution at 20° are given in Table I.

It may now be stated with certainty that increasing the weight of the aryl groups in a hexa-

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(1) This is the fifth paper in the series. For the fourth paper see THIS JOURNAL, **59**, 1176 (1937).

(2) Copenhaver, Roy and Marvel, *ibid.*, **57**, 1311 (1935).

(3) Taylor, *ibid.*, **48**, 858 (1926).

(4) Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935).

(5) Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922).