1018. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XX.[1] Acetoxychloride Adducts from the Chlorination of Phenanthrene in Acetic Acid.*

By P. B. D. DE LA MARE and R. KOENIGSBERGER.

The chlorination of phenanthrene by chlorine in acetic acid, or by chlorine acetate in acetic acid, is accompanied by the formation of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene, one of the geometrical isomers of which has been isolated and characterised kinetically and by thin-layer chromatography. It decomposes on heating to acetoxyphenanthrene and chlorophenanthrene. It is considered to be the *trans*-isomer, from the products of its reaction with silver acetate in acetic acid. The presence also of its geometrical isomer is inferred. The significance of these observations is discussed in relation to the reaction-paths involved in chlorination and to addition–elimination sequences leading to aromatic substitution.

THE reaction of chlorine with phenanthrene in acetic acid gives [2] 9-chlorophenanthrene (*ca.* 34%), and *cis*- and *trans*-9,10-dichloro-9,10-dihydrophenanthrene (*ca.* 42%). It was considered also, from analytical evidence, that acetoxychlorides (*ca.* 14%) are formed, but these were not isolated or properly characterised, and the remainder of the chlorine consumed in the reaction was not accounted for. In reactions of halogens with olefins or aromatic compounds in acetic acid, the formation of acetoxychloride adducts, followed by elimination of hydrogen chloride, results in the introduction of an acetoxyl substituent:

$$\tag{1}$$
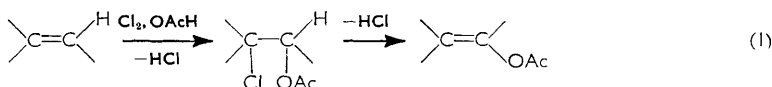
Various reports [3,4] of acetoxylations and benzoyloxylations accompanying electrophilic substitution in aromatic systems focus attention on possible routes by which electrophilic acetoxylation can be effected. The above addition–elimination sequence is one such route, and the present work establishes conditions under which such a path accompanies chlorination of phenanthrene.

EXPERIMENTAL

Light petroleum had b. p. 40—60°. Some materials and methods have been described.[cf. 1,2] Phenanthr-9-yl methyl ether was prepared by Fieser, Jacobson, and Price's method,[5] through the reaction of bromine with phenanthrene in methanol containing sodium acetate; it was demethylated with hydrogen bromide to give phenanthr-9-ol, m. p. 153°. We were unsuccessful[cf. 6] in obtaining the yields recorded by the original investigators. 9-Acetoxyphenanthrene was prepared by acetylation of phenanthrol with acetic anhydride. After recrystallisation from aqueous ethanol its m. p. was 78°. Its ultraviolet absorption spectrum with maxima at $\lambda = 3500$ Å (ε, 280), $\lambda = 3410$ Å, $\lambda = 3325$ Å (ε, 320), $\lambda = 3255$ Å, $\lambda = 3175$ Å, $\lambda = 2970$ Å (ε, 10,900), $\lambda = 2850$ Å, $\lambda = 2765$ Å, $\lambda = 2530$ Å (ε, 57,000), $\lambda = 2140$ Å (ε, 32,000), shows a marked resemblance to those of the known chlorophenanthrenes. The isomeric 9,10-dichloro-9,10-dihydrophenanthrenes were prepared for reference as before.[2] When reaction-mixtures containing the *cis*-isomer are chromatographed on silica gel, this compound is eluted by light petroleum after phenanthrene and 9-chlorophenanthrene. It is destroyed, however, by chromatography on alumina, whereas the *trans*-isomer is destroyed on silica gel, but can be recovered from alumina.

[1] Part XIX, de la Mare, Johnson, and Lomas, preceding Paper.
[2] de la Mare and Klassen, *Chem. and Ind.*, 1960, 498; de la Mare, Klassen, and Koenigsberger, *J.*, 1961, 5285.
[3] Fischer, Packer, Vaughan, and Wright, *Proc. Chem. Soc.*, 1961, 369.
[4] Bryce-Smith, *Nature*, 1953, **172**, 863; Bryce-Smith and Clarke, *J.*, 1956, 2264.
[5] Fieser, Jacobson, and Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2163.
[6] Hunsberger, Ketcham, and Gutowsky, *J. Amer. Chem. Soc.*, 1952, **74**, 4839.

Thin-layer Chromatography.—Some of the products of chlorination of phenanthrene could be separated by thin-layer chromatography on silica gel (" G," Merck) by Stahl's technique.[7] For qualitative work the method described by Lees and de Muria,[8] involving no elaborate apparatus, was adequate. The components could be seen under ultraviolet light (Hanovia Chromatolite), or detected by spraying with diazotised *p*-nitroaniline, with silver nitrate sensitised with fluorescein, or with vanillin and sulphuric acid in absolute ethanol followed by heating to 120°. With light petroleum as solvent, chlorophenanthrene, phenanthrene, and dichlorodihydrophenanthrene were separated in that order, while the oxygenated material remained at the origin. With benzene, a component appeared as a characteristic spot (R_F, 0·7) which appeared light yellow with the silver nitrate–fluorescein reagent; part of this was later identified (see below) as an acetoxychlorodihydrophenanthrene. 9-Acetoxyphenanthrene, (R_F, 0·6) and phenanthrol (R_F, 0·3) gave black spots; the latter appeared instantaneously, whereas the former developed slowly.

trans-9-*Acetoxy*-10-*chloro*-9,10-*dihydrophenanthrene.*—(a) *Isolation.* In early experiments, chromatography on silica gel in light petroleum followed by benzene was used to separate the products of chlorination of phenanthrene. A 9-acetoxy-10-chloro-9,10-dihydrophenanthrene was isolated as a tacky syrup, often contaminated with acetoxyphenanthrene. Adducts showing very similar infrared spectra were obtained from chlorinations in which molecular chlorine or hypochlorous acid in 80% acetic acid were used.

Later it was found that a white crystalline adduct with a similar infrared spectrum could be isolated from the reaction mixture by chromatography on suitably deactivated alumina. This method was used for the preparation of material for most of the quantitative work described below.

Chlorine (about 100 millimoles) in glacial acetic acid was added to phenanthrene (25 g.) in glacial acetic acid (total volume about 400 ml.) in the dark. The mixture was left overnight and was then added to ether. The solution was washed with water until the washings gave no turbidity with silver nitrate and were no longer acid to methyl orange. Free chloride was rapidly removed, but a large volume of water was needed to remove the last traces of acetic acid. Ether was removed from the solution containing the organic reaction product by distillation under reduced pressure. The pale yellow oily residue was suspended in a solution of 10% ether in light petroleum and chromatographed on alumina (M. & B. " for chromatography," *ca.* 500 g.) which had been shaken for 4 hr. with 3% by weight of water. It had been found that the required material was destroyed unless the alumina was sufficiently deactivated by water. The critical concentration of water is reached when, on packing the column, the alumina no longer adheres to the glass. The first 450 ml. of eluate contained chlorophenanthrene and phenanthrene; the following 300 ml. contained *trans*-dichloride, identified by thin-layer chromatography and by its infrared spectrum. The solvent was changed to 20% ether in light petroleum. No significant amount of adduct was found in the next 850 ml. The acetoxy-chloro-adduct was eluted in the following 450 ml. The solvent was distilled off under reduced pressure and the white crystalline material was recrystallised by dissolving it in the minimum of ether and adding light petroleum. There was obtained 0·9 g. (yield, 3%), m. p. 101° (Kofler hot-stage apparatus). Further recrystallisation from ethanol gave a product of m. p. 104° (Found: C, 70·0; H, 4·6; Cl, 13·2; O, 11·9. $C_{16}H_{13}ClO_2$ requires C, 70·5; H, 4·8; Cl, 13·0; O, 11·7%). Its infrared spectrum and those of a number of related compounds are given in the Table. The spectra, which refer to mulls in Nujol, were recorded on a Grubb–Parsons DB1 recording spectrophotometer.

(b) *Reaction with alkali.* The reaction of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene with alkali could be followed by titration in a mixture of benzene and methanol essentially as described by Yacubik, Safranski, and Mitchell.[9] By using a glass electrode, with a silver electrode as reference, and 0·01N-potassium methoxide in benzene–methanol, two well-separated inflections were obtained for hydrochloric and acetic acid. Direct plots of e.m.f. against volume of added alkali were used; with our set-up the plots had the normal S-shape (cf. ref. 9). The alkali was standardised separately against hydrochloric acid and benzoic acid; slight differences in the normality factors were observed.

It could be shown that, when the liberation of chloride had reached 94%, that of acetic

[7] Stahl, Schröter, Kraft, and Reuz, *Pharmazie*, 1956, **11**, 633.
[8] Lees and De Muria, *J. Chromatog.*, 1962, **8**, 108.
[9] Yacubik, Safranski, and Mitchell, *Analyt. Chem.*, 1958, **30**, 1741.

Infrared absorption bands (cm.$^{-1}$; range 600—1800 cm.$^{-1}$) of
9-acetoxy-10-chloro-9,10-dihydrophenanthrene and derived materials.

trans-9-Acetoxy-10-chloro-9,10-dihydro-phenanthrene	cis-9,10-Diacetoxy-9,10-dihydro-phenanthrene	trans-9,10-Diacetoxy-9,10-dihydro-phenanthrene	cis-9-Acetoxy-10-hydroxy-9,10-dihydro-phenanthrene	9-Acetoxy-phenanthrene	Phenanthr-9-ol
696sh	700m	734s	734s	724s	725s
702m	712w	763s	744s	748s	746s
734s	734s		762m	758s	762s
	746w	787w	789w	771s	790w
760m	770m				
	783m				
813w					839w
920w		855w			871w
944w	912m	937m	935w	907w	881w
	935w	954m	944w	926w	945w
954m	942m	972sh			
			1021m		
1010m	1012m	1018s	1030m	1034w	1031w
1050w	1031m				
	1050w		1050m	1065s	1067s
	1090m		1083m		
			1097m		
1150w	1120w	1129w		1106w	1107w
		1159w		1148m	1144w
1163w	1167w				
1188w		1185w		1159m	
	1204m				
1219sh	1211m	1220s	1202w	1168m	
1230s	1222s	1235s	1243s	1208s	1221w
	1241s		1250sh	1227s	1232w
			1286w		1277w
1310w	1345w	1308w	1336w	1305m	1346w
1370NJ	1368NJ	1350w		1374NJ	1374NJ
		1368NJ	1373NJ		
1450NJ	1450NJ	1449NJ	1450NJ	1453NJ	1460NJ
				1460NJ	
	1520sh				1600w
					1626m
1733s	1728s	1739s	1731s	1751s	

s = Strong; m = medium; w = weak; sh = shoulder; NJ = Nujol bands.

acid had proceeded to no more than 2%. It is therefore possible to measure the rate of dehydro-chlorination by estimating the chloride liberated, without reference to the hydrolysis of the acetate group.

In a kinetic experiment at 0°, the material obtained by chromatography on alumina (0·2737 g., 0·993 mM) was dissolved in ethanol (96%) and made up to 100 ml. Aliquot portions (10 ml.) of this solution were mixed with 10 ml. of 0·0378N-potassium hydroxide in ethanol (96%), and the chloride liberated was determined, as follows:

Time (min.)	3	6	9	12	24	48	72	∞
HCl liberated (ml. 0·01080N)	1·41	2·26	3·12	3·87	5·82	7·66	8·83	9·93
k_2 (l. mole^{-1} min.$^{-1}$)	2·87	2·59	2·56	2·56	2·45	2·31	2·77	—

By using samples of the syrup isolated by chromatography on silica gel, it was shown that liberation of chloride by alkali at 0°, as determined by titration against silver nitrate, has a rate coefficient (k_2) decreasing from 3·6 l. mole^{-1} min.$^{-1}$ (37% reaction) to 2·8 l. mole^{-1} min.$^{-1}$ (92% reaction). This result suggests that such samples contain a small amount of a more reactive isomer. Further indications in the same direction have also been obtained; thus bulked fractions of the acetoxychloride, separated by relatively large-scale chromatography on silica gel, gave acetoxyphenanthrene and chlorophenanthrene in the ratio of 10 : 1 on vapour-phase chromatography; if these samples were allowed to stand at room temperature for some weeks, the value fell to *ca.* 4 : 1. This result indicates the presence of an isomer which decomposes on heating to give a much greater proportion of acetoxyphenanthrene than is given by the purified material.

(c) *Decomposition by heat.* A portion of the purified 9-acetoxy-10-chloro-9,10-dihydro-phenanthrene was heated (30 min.) under nitrogen *in vacuo* at 180°. The products were separated by chromatography on silica gel. Chlorophenanthrene, identified by its characteristic infrared spectrum, and 9-acetoxyphenanthrene, identified by its infrared spectrum and m. p. (78°) after recrystallisation, were obtained in the ratio 1 : 2 by weight.

(d) *Vapour-phase chromatography.* 9-Acetoxyphenanthrene on vapour-phase chromatography under conditions suitable for separating mono- and di-chlorophenanthrenes [cf. 10] gave a peak which fell between these groups of substances. Vapour-phase chromatography of either the crude product of chlorination of phenanthrene or fractions rich in 9-acetoxy-10-chloro-9,10-dihydrophenanthrene gave a peak corresponding with 9-acetoxyphenanthrene. The corresponding material was collected and identified as 9-acetoxyphenanthrene by its m. p. (77—78°) and its ultraviolet spectrum. The purified *trans*-9-acetoxy-10-chloro-9,10-dihydro-phenanthrene under these conditions gave acetoxyphenanthrene and chlorophenanthrene in the ratio 4 : 1.

(e) *Reaction with silver acetate in acetic acid.* For characterisation of the products of solvolysis of 9-chloro-10-acetoxy-9,10-dihydrophenanthrene in acetic acid in the presence of silver acetate, we were fortunate to have, through the courtesy of Professor E. E. Turner, a sample of the menthoxy-acetate [11] of the relevant *trans*-diol, from which was prepared trans-9,10-diacetoxy-9,10-dihydrophenanthrene; and through the courtesy of Professor E. Boyland, of the *cis*-diol,[11] from which was prepared *cis*-9,10-diacetoxy-9,10-dihydrophenanthrene. These compounds could be distinguished clearly by their infrared spectra, which are recorded in the Table.

A number of preliminary experiments were made to establish the best conditions for solvolysis of the acetoxychloro-adduct. In the first of these, by reaction in acetic acid with excess of solid silver acetate at 110°, both *cis*- and *trans*-9,10-diacetoxy-9,10-dihydrophenanthrene were detected in the product, but most of the reaction resulted in elimination. More satisfactory results were obtained at low temperature with dissolved silver acetate. The crystalline acetoxychloro-adduct, 0·4364 g. (1·6 millimoles) in dry, purified acetic acid (50 ml.), was added to a saturated solution of silver acetate (400 ml. 0·0056N) and left for 4 days at 30°. The solution was filtered through a weighed sintered glass crucible and the precipitate was washed with glacial acetic acid. The washings were added to the filtrate. The precipitate was then washed with dilute nitric acid, dried at 120°, and weighed; it was silver chloride, (0·2196 g.), equivalent to 0·417 g. (95%) of the adduct used. Acetic acid was evaporated from the filtrate under reduced pressure. The residue was suspended in the minimum amount of light petroleum and chromatographed on a column of 40 g. silica gel (Hopkin and Williams, M.F.C.). After being washed with light petroleum (30 ml.) and a mixture (1 : 1) of benzene and light petroleum, the solvent was changed to benzene. 9-Acetoxyphenanthrene (0·0598 g.; 16%) was quickly eluted, followed by a yellow band which yielded an unidentified orange solid (0·006 g.). The column was then eluted with ether. The ether eluate contained cis-9-*acetoxy*-10-*hydroxy*-9,10-*dihydro-phenanthrene* (0·308 g., 76%), which after recrystallisation from a mixture of ether and light petroleum had m. p. 113° (Found: C, 75·7; H, 5·6; O, 19·0. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5; O, 18·9%). On acetylation it gave *cis*-9,10-diacetoxy-9,10-dihydrophenanthrene, with infrared spectrum identical with that of authentic material.

A similar experiment was carried out, the acetolysis being performed in a solvent containing 1% of water. *cis*-9-Acetoxy-10-hydroxy-9,10-dihydrophenanthrene, identified by its infrared spectrum, was obtained from the reaction mixture in 74% yield. Most of the remainder consisted of 9-acetoxyphenanthrene, detected in the eluate by thin-layer chromatography.

The second-order rate-coefficients, k_2, for the acetolysis of the acetoxychloride adduct, the *cis*-dichloride, and the *trans*-dichloride (0·0023, 0·0027, 0·0025M respectively) with silver acetate (0·0027, 0·0029, 0·0027M respectively) in acetic acid at 30° were 0·40, 0·40, and 0·17 l. mole^{-1} min.$^{-1}$ respectively.

The products of acetolysis of the three adducts were compared by thin-layer chromatography on silica gel (" G," Merck) with benzene as solvent and vanillin–sulphuric acid as the spray-reagent. The acetoxychloride, after treatment with silver acetate in anhydrous acetic acid, evaporation to dryness under reduced pressure, and solution of the organic material in acetone, still contained some unchanged acetoxychloride, together with 9-acetoxyphenanthrene, phen-anthrol, a trace of a 9,10-diacetoxy-9,10-dihydrophenanthrene (the isomers are not separated

[10] Cf. Beaven, James, and Johnson, *Nature*, 1957, **179**, 490.
[11] Booth, Boyland, and Turner, *J.*, 1950, 1188, 2808.

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under these conditions) and 9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene. The 9,10-di-acetoxy-9,10-dihydrophenanthrenes, after the same treatment, were substantially unchanged; a trace of 9-acetoxyphenanthrene could be detected in the solution of the *cis-*, and a trace of the acetoxyhydroxy-compound in that of the *trans-*isomer.

Analysis by Isotope Dilution.—The method of isotopic dilution was used to determine the amount of the crystalline 9-acetoxy-10-chloro-9,10-dihydrophenanthrene formed in the reaction of phenanthrene with chlorine in acetic acid. The general procedure has been described in earlier Papers.[cf. 12] The specific activity of chloride solutions was determined by conversion into silver chloride and reduction in a stream of hydrogen at about 600°. The resulting hydro-chloric acid was absorbed in water; its specific activity was determined as a ratio of counts per minute to normality, the latter being determined by potentiometric titration with silver nitrate. Appropriate correction was made for background. Solutions of molecular chlorine were converted into chloride with sodium metabisulphite. Phenanthrene (8·8 millimoles) was allowed to react with chlorine ($^{36}Cl_2$, 2·86 millimoles, specific activity of derived chloride, 8·03 × 10^5 counts min.$^{-1}$ mole^{-1}) in acetic acid (90 ml.). After the reaction was complete, inactive *trans-*9-acetoxy-10-chloro-9,10-dihydrophenanthrene (0·7637 g., 2·80 millimoles) was added, and the total acetoxychloro-adduct was isolated as described above. The specific activity of the hydrolysate of this product was 1·056 × 10^5 counts min.$^{-1}$ mole^{-1}, unchanged within experimental error on re-chromatography. From this result it can be calculated that 14·9 ± 0·3% of the chlorine used in the reaction had been converted into the crystalline *trans-*9-acetoxy-10-chloro-9,10-dihydrophenanthrene; the limits given are those of statistical probable error of counting.

DISCUSSION

Structure of the Crystalline Acetoxychloride Adduct.—It is clear that one of the components of the product of chlorination of phenanthrene by chlorine in acetic acid (where the electrophilic reagent is molecular chlorine [cf. 13]) or by hypochlorous acid in aqueous acetic acid (where the electrophilic reagent is considered [14] to be chlorine acetate) is 9-acetoxy-10-chloro-9,10-dihydrophenanthrene. Part of this can be purified by chromatography, and when so purified is reasonably stable. It is hydrolysed by alkali very rapidly; second-order rate-coefficient, $k_2 = ca.$ 2·5 l. mole^{-1} min.$^{-1}$ in ethanol at 0°. This value is less than that for *cis-*9,10-dichloro-9,10-dihydrophenanthrene ($k_2 = ca.$ 160 l. mole^{-1} min.$^{-1}$ at 0° in ethanol), but it is very much greater than that for *trans-*9,10-dichloro-9,10-dihydrophenanthrene, which reacts at a negligible speed at 0° ($k_2 = 0·02$ l. mole^{-1} min.$^{-1}$ at 58·7°).[2]

We have determined the configuration of this adduct by determining the steric course of its reaction with silver acetate in acetic acid. Winstein and his co-workers [15,16] have shown that *trans-*1-acetoxy-2-chlorocyclohexane (I) can react with silver acetate in acetic acid at *ca.* 100° in various ways, the most important of which are: (*a*) in dry acetic acid, with overall retention of configuration, when the product is *trans-*1,2-diacetoxycyclohexane (IV); (*b*) in acetic acid containing a little water, with overall inversion of configuration, when the product is *cis-*1-acetoxy-2-hydroxycyclohexane (V). It was made probable that the *ortho-*ester (VI) is an intermediate, and its various alternative reactions were established; for example, when the solvolyses leading to (VI) are carried out in the absence of a base, a path from (VI) to *cis-*diacetoxycyclohexane is apparently available.

The essential feature of these reaction-sequences (Scheme 1) depends on the possibility of internal nucleophilic displacement (neighbouring-group participation) by the acetoxy-group, which must be *trans* to the leaving chlorine. The *cis-*isomer reacts more slowly, to give predominantly products of elimination.

The conditions adopted in our experiments on 9-acetoxy-10-chloro-9,10-dihydrophen-anthrene involved the use of much more dilute solutions than those available to Winstein

[12] de la Mare and Pritchard, *J.*, 1954, 3910.
[13] de la Mare, in " Theoretical Organic Chemistry," Kekulé Symposium, Butterworths, London, 1958, p. 219.
[14] de la Mare, Hilton, and Varma, *J.*, 1960, 4044.
[15] Winstein and Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2780, 2787; Winstein, Hess, and Buckles, *ibid.*, p. 2796.
[16] Cf. Winstein, Grunwald, and Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.

and his co-workers for the acetoxychlorocyclohexanes; for our reactions were much more rapid, proceeding smoothly at 30°. The greater reactivity of our system is to be expected,
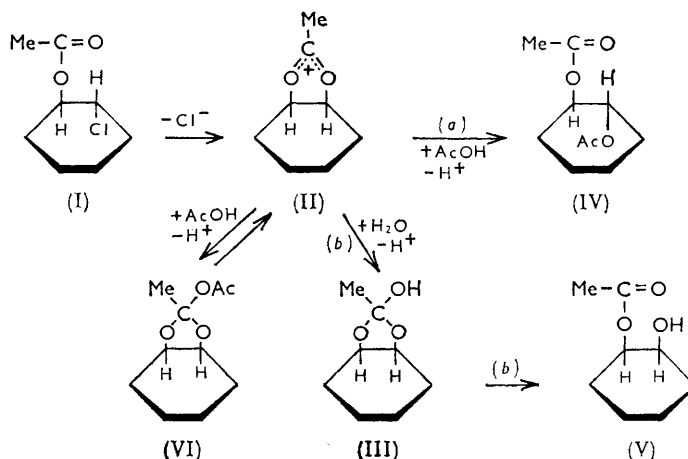
Scheme 1.   Silver-ion-catalysed acetolysis of *trans*-1-acetoxy-2-chlorocyclohexane.

since the aryl group will stabilise the development of carbonium ionic character on the carbon atom from which the chlorine atom is heterolysed. The driving force for elimination must, however, be much increased also; not only because the adjacent electron-withdrawing aryl groups facilitate proton-loss, but also because of the aromatic stability gained by forming the phenanthrene system.

All our solvolyses were catalysed by silver acetate, and so (since silver chloride is precipitated during the reaction and hence silver acetate is removed) gave satisfactory second-order rate-coefficients. The reactions of *cis*- and of *trans*-9,10-dichloro-9,10-di-hydrophenanthrene gave almost entirely products of elimination. The more rapid reaction of the *cis*-isomer may involve synchronous removal of hydrogen and chlorine, but this is unlikely for the *trans*-isomer. Displacement processes are negligible under these conditions for the dichlorides.

By contrast, the reaction of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene gives mainly the product of displacement, and so this type of reaction must be considerably faster for the acetoxychloride than for the dichlorides. Consideration of the effect expected for chlorine and acetoxyl on displacement of chlorine in the absence of neighbouring-group participation suggests that these two groups should have qualitatively similar effects; their inductive influences, as measured for example by the dissociation constants of substituted benzoic acids ($\sigma_m = 0.37$ and 0.39, respectively) [17] are nearly the same. The reactivity of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene, therefore, requires for its interpretation the postulate that the neighbouring acetoxyl group is participating in the rate-determining stage of the solvolysis. This can happen only if the acetoxyl group is *trans* to the departing chlorine (VII; Scheme 2).

This conclusion is supported by the nature of the products isolated from the solvolysis. Under our conditions we obtained evidence for reaction to form diacetates (cf. path (*a*), Scheme 1) only under forcing conditions similar to those adopted by Winstein and his co-workers.[15] Under the conditions of the kinetic experiments, the hydroxyacetate (X; Scheme 2), was isolated in *ca.* 70% yield. In the experiment without deliberately added water, it is possible that the *ortho*-ester (IX) was formed, and that the final product was obtained only by decomposition of this when water was added in working up the reaction mixture. The overall steric course of the reaction and the yield of the *cis*-hydroxyacetate were not significantly altered by carrying out the reaction in the presence of deliberately

[17] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

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added water. The only other substantial component of the reaction-product was 9-acetoxy-phenanthrene (XI), obtained no doubt by dehydrochlorination catalysed by silver acetate.

It was shown in independent experiments that the 9,10-diacetoxy-9,10-dihydrophenanthrenes were essentially stable under the conditions used for the acetolyses.* The only reasonable interpretation of the course of acetolysis of our acetoxychloride, therefore, is that it is the *trans*-isomer (VII), which on solvolysis in acetic acid containing silver acetate forms a cyclic intermediate (VIII) which ring-opens with water to give *cis*-9-acetoxy-10-hydroxy-9,10-dihydrophenanthrene (X); inversion of configuration is therefore the overall result.

Intermediates in the Electrophilic Chlorination of Phenanthrene.—In an earlier Paper [2] we reported from analytical data that chlorination of phenanthrene in acetic acid gives 14% of an acetoxychloride. Analysis by isotopic dilution has now shown that 15% of *trans*-9-acetoxy-10-chloro-9,10-dihydrophenanthrene is formed; a substantial part of this can be isolated by careful chromatography of the product of reaction. The implication that the acetoxychloride adduct produced in the chlorination is wholly of the *trans*-configuration is not, however, certain. We believe that up to about 5% of the *cis*-isomer may also be formed, but if it is formed, that it is too labile for isolation by our
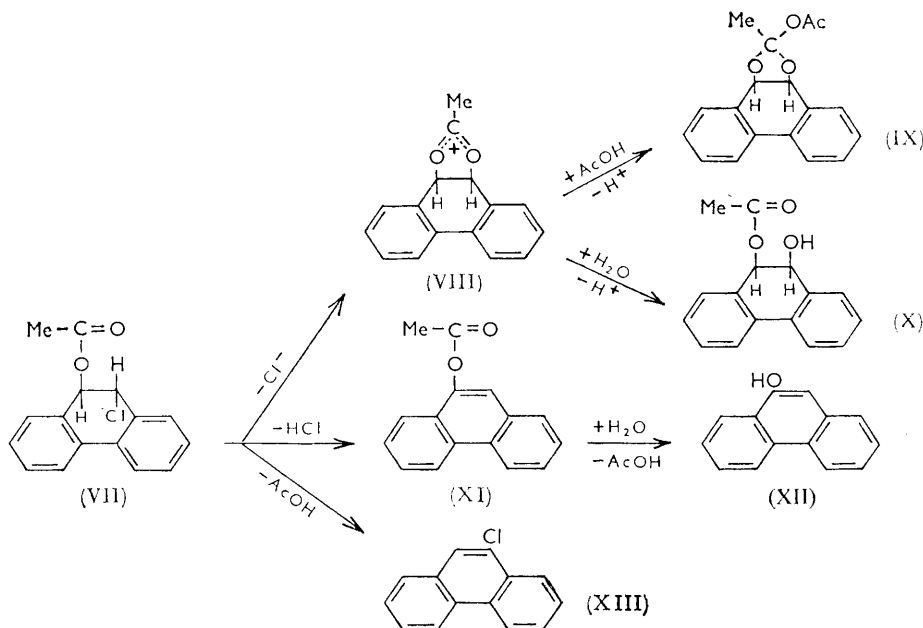
Scheme 2. Some reactions of 9-acetoxy-10-chloro-9,10-dihydrophenanthrene.

methods. Our reasons are indicated in the experimental section; further work is in progress, and will be reported later, on the effects of added electrolytes on the proportions of the various components of the reaction mixtures, and these should help to throw further light on this problem. One important point that seems quite clearly established, however, is that the main acetoxychloride produced in chlorination in acetic acid contains a considerable excess of the *trans*-isomer. This is, of course, the stereochemistry expected for a two-stage addition in which the entering electrophilic chlorine protects the adjacent carbonium ionic centre from attack by the nucleophile on the same side of the double

* The facts that the *trans*-diacetate gave a trace of hydroxyacetate and the *cis*-isomer a trace of acetoxyphenanthrene give further support to our assessment of the structure of the acetoxychloride adduct.
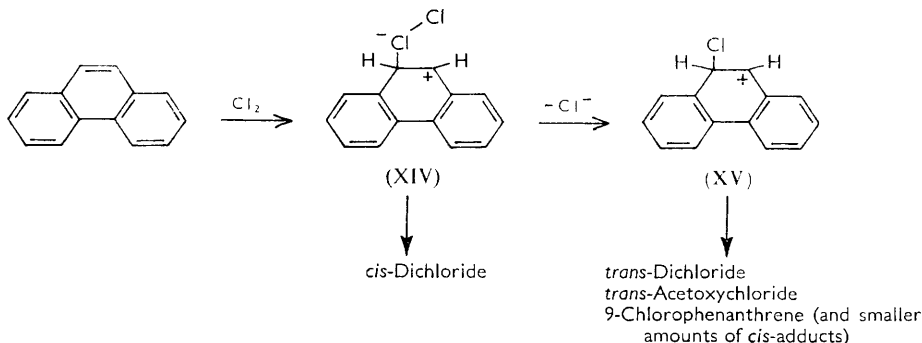
Scheme 3. Possible reaction path in the chlorination of phenanthrene.

bond;[18] the result, however, is in very marked contrast with that for the concomitant addition of chlorine, for which the *cis*-isomer predominates. The results are consistent with the view[2] that the formation of the *cis*-dichloride is determined at an early stage in the reaction path, perhaps through the intermediate (XIV), whereas the *trans*-adducts are derived at a later stage, perhaps through a different intermediate (*e.g.*, XV).

Pyrolysis of trans-9-*Acetoxy*-10-*chloro*-9,10-*dihydrophenanthrene.*—The thermal, gaseous, unimolecular decompositions of acetates are usually faster than those of chlorides.[19] In the present system, however, hydrogen chloride is lost more readily than acetic acid, since acetoxyphenanthrene predominates over chlorophenanthrene in the product of pyrolysis. These reactions must both be *cis*-eliminations; it may be that the four-centre transition state for loss of hydrogen chloride is favoured by considerations of entropy over the six-centre transition state for loss of acetic acid.

It seems that the corresponding *cis*-isomer, with hydrogen atoms *trans* to both the chlorine and the acetoxyl substituent, gives an even greater proportion of 9-acetoxyphenanthrene on pyrolysis; since the oily acetoxychloride adduct isolated in early experiments almost certainly contained this isomer, and gave on pyrolysis acetoxyphenanthrene and chlorophenanthrene in a ratio greater than 10 : 1. The *cis*-isomer seemed also to be the more labile to acid-catalysed hydrolysis, probably giving first 9-chloro-10-hydroxy-9,10-di-hydrophenanthrene, which rapidly loses hydrogen chloride and gives phenanthrol.

Addition–elimination Sequences Associated with Electrophilic Attack on Aromatic Compounds.—The present experiments establish the importance, for chlorination of phenanthrene in acetic acid, of a reaction path of the addition–elimination type (eqn. 1), the adducts in this case being in part unstable even under the most cautious working-up procedures that we have been able to employ, and in part stable to these conditions, though unstable to heat. The amount of product appearing from this route depends critically on the method of working-up; from the results of vapour-phase chromatography, for example, one would deduce that about 20% of acetoxylation accompanies chlorination of phenanthrene in acetic acid.

Rates and products of electrophilic aromatic substitutions are commonly discussed in terms of intermediates (*e.g.*, XVI) formed by attachment of an electrophil (E) to the aromatic system with consequent development of a carbonium-ionic centre.[20] The substitution is then completed by proton-loss, and various degrees or types of bonding between the electrophil and the aromatic nucleus can be envisaged.[21-23] Even this simple mechanism can lead to considerable complexities in the reaction path.[24]

[18] Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947.
[19] Cf. Barton and Howlett, *J.*, 1949, 165; Blades, *Canad. J. Chem.*, 1954, **32**, 366.
[20] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.
[21] Dewar, *J.*, 1946, 406, 777.
[22] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[23] R. D. Brown, *J.*, 1959, 2224.
[24] Zollinger, *Experientia*, 1956, **12**, 165.

Theoretical discussions often neglect the function of the associated nucleophil, probably because this usually,[25,26] though not invariably,[26,27] does not participate in the removal of the proton. There are various other ways, however, in which the nucleophil can play a vital role in the reaction. Elsewhere [cf. 13] we have emphasised that the formation of intermediates with structures such as (XVII) may have important consequences in determining, *inter alia*, the response of the system to change in structure. Proton-loss from other parts of the molecule [28,29] may lead to complicated reaction-sequences involving double-bond migrations.

(XVI)   (XVII)
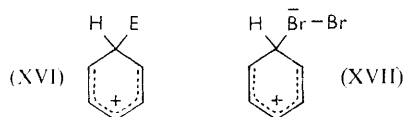
The present work illustrates some further aspects of a third role [2,13] which can be played by the nucleophil, whether derived directly from the reagent or from the environment; if, in competition with any of the processes already mentioned, it can complete addition to the aromatic system by combining with the developing carbonium ionic centre. The formation of predominantly *cis*-dichloride is most easily rationalised in terms of a very specific geometry for the transition state. The formation of acetoxychloride, of which the most easily isolated component is the *trans*-isomer, comes about through diversion of an intermediate by reaction with the solvent.

The chlorination of phenanthrene to form chlorophenanthrene, therefore, does not necessarily proceed through an addition–elimination sequence, though it is possible to choose conditions of working-up which ensure that part is formed in this way. The accompanying acetoxylation, on the other hand, necessarily must go through such a path. Corresponding conclusions have been reached for other reactions of phenanthrene with electrophils. Thus Price [30] has shown that the bromination of phenanthrene does not necessarily involve 9,10-dibromo-9,10-dihydrophenanthrene; whereas methoxylation of phenanthrene [5] must involve 9-bromo-10-methoxy-9,10-dibromophenanthrene (XVIII), thus:

(XVIII)
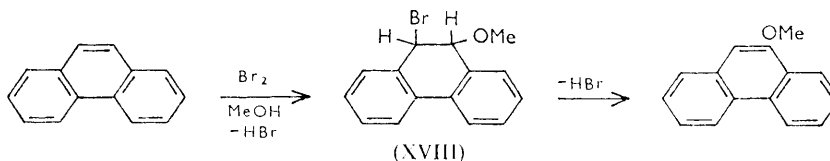
It is difficult to assess from the data available whether the acetoxylations [3] and benzoyl-oxylations [4] which have been observed to accompany electrophilic nitrations and halogenations of benzene derivatives could have arisen in a similar way. For derivatives of benzene it would normally be expected that the cyclohexadienes (*e.g.*, XIX) produced by 1,2- addition initiated by electrophilic halogen would undergo rapid further reaction at the double bond, so that addition–elimination sequences give di- or tri-substituted derivatives. This is the situation for the chlorination of biphenyl; [31] and we have shown recently [32] that tetra-chloride and acetoxytrichloride adducts are formed in the reaction of naphthalene and of 2-methylnaphthalene with chlorine in acetic acid. It is by no means so clear, however, what would be the situation for a 1,4-adduct (*e.g.*, XX). In such a compound the double

[25] Hughes, Ingold, and Reed, *J.*, 1950, 2400.
[26] Melander, *Arkiv Kemi*, 1950, **2**, 211.
[27] Grovenstein and Kilby, *J. Amer. Chem. Soc.*, 1957, **79**, 2972.
[28] Plant and Tomlinson, *J.*, 1933, 955.
[29] Bachiocchi and Illuminati, *Gazzetta*, 1962, **92**, 89; *Tetrahedron Letters*, 1962, **15**, 637.
[30] Price, *J. Amer. Chem. Soc.*, 1936, **58**, 1934, 2101; *Chem. Reviews*, 1941, **29**, 37.
[31] Beaven, de la Mare, Hassan, Johnson, and Klassen, *J.*, 1961, 2749.
[32] de la Mare, Koenigsberger, and Lomas, unpublished work.

bonds are isolated and are deactivated by the adjacent substituents. The reversibility of the whole addition process may for bromine and iodine make the diversion of the reaction

(XIX)   (XX)
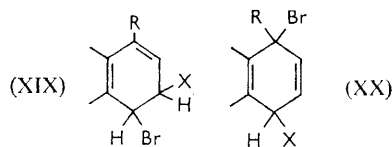
to products of elimination a reaction path more readily available than for chlorination; 1,4-elimination of HBr from such a structure as (XX) might well in some cases compete with 1,2-elimination of HX from (XIX).