1045. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XI.*[1] *Chlorination of Phenanthrene in Acetic Acid.*

By P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger.

Phenanthrene and chlorine in acetic acid give 9-chlorophenanthrene as the main product of substitution, but the reaction is accompanied by addition which accounts for more than 40% of the chlorine consumed and gives mainly *cis*-9,10-dichloro-9,10-dihydrophenanthrene, which is much more reactive than the *trans*-isomer with alkali. About 10% of the reaction gives an acetoxychlorodihydrophenanthrene. No evidence of the participation of homolytic processes was obtained. The results are interpreted as further evidence that intermediates of the type $ArHCl_2$, involving halogen with an expanded octet, are important in aromatic substitution.

The discovery[1] that a part of the reaction of chlorine with biphenyl in acetic acid involves addition to the aromatic nucleus led us to consider whether analogous processes would be found for other, chemically related compounds.

Phenanthrene is well known to undergo addition across the 9,10-positions accompanying substitution, and such processes have often[2] been regarded as involving alternative fates of a common intermediate, although for chlorination no detailed study has been made to establish this matter.[3] Sandqvist[4] obtained 9-chlorophenanthrene, m. p. 53°, and a 9,10-dichloro-9,10-dihydrophenanthrene, m. p. 157°, as products of reaction of phenanthrene with one mol. of chlorine. A more detailed study of this reaction comprises the main part of the investigation now reported. A preliminary account has been given elsewhere.[5]

Experimental

Some of the materials and methods have been described in previous Parts of this series.[6] Phenanthrene was purified by treatment with maleic anhydride.[7] 9-Chlorophenanthrene after repeated recrystallisation from aqueous ethanol had m. p. 53—53·5°. Sandqvist[4] had previously reported the preparation of *trans*-9,10-dichloro-9,10-dihydrophenanthrene, m. p. 156—157°, as a compound of then unknown stereochemistry. We obtained it in very poor yield by treating phenanthrene with chlorine in chloroform. After removal of solvent, the product was dissolved in ethanol, and sodium ethoxide was added until no more was rapidly consumed (lacmoid as indicator). The organic product was precipitated with water, filtered off, and washed several times with light petroleum. It was then recrystallised many times from benzene–light petroleum; the infrared spectrum and chemical behaviour of specimens of m. p. 146° and upwards seemed to be little changed by further purification.

Chlorination in the presence of benzoyl peroxide gave a much purer product. To a solution of phenanthrene (100 g.) and benzoyl peroxide (1 g.) in dry chloroform (200 ml.) was added a slight deficiency of chlorine in chloroform. The solution was left overnight and then shaken with alcoholic sodium ethoxide to remove the *cis*-isomer. The solution was washed with dilute hydrochloric acid and with water, then passed through an alumina column to remove benzoyl peroxide. Most of the chloroform was removed *in vacuo*, and a solid product was precipitated from it by adding light petroleum and cooling the mixture to −78°. The sticky precipitate was washed repeatedly with light petroleum, and the residue was recrystallised several times by cooling, to 5°, a solution in chloroform saturated at 30°. The yield was 6·6 g. The compound decomposes rapidly at or near the m. p. (157°), which was determined by holding

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[1] Part X, Beaven, de la Mare, Hassan, Klassen, and Johnson, *J.*, 1961, 2749.

[2] Cf. Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2101; *Chem. Rev.*, 1941, **29**, 37.

[3] Cf. de la Mare and Ridd, "Aromatic Substitution—Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, p. 174.

[4] Sandqvist, *Annalen*, 1918, **417**, 17; Sandqvist and Hagelin, *Ber.*, 1918, **51**, 1515.

[5] de la Mare and Klassen, *Chem. and Ind.*, 1960, 498.

[6] Cf. de la Mare and Hassan, *J.*, 1958, 1519.

[7] Cf. *Org. Synth.*, 1948, **28**, 19; 1954, **34**, 31.

the m. p. block at a steady temperature and inserting a freshly filled capillary. Fusion in less than 1 min. was considered genuine.

In the course of some days the compound decomposed at room temperature, but it could be stored for long periods at −80°; on being heated, it gave hydrogen chloride and 9-chlorophenanthrene.

The stereochemistry is indicated by its relatively small reactivity with alkali, and was proved by partial asymmetric decomposition with brucine—Cristol, Stermitz, and Ramey's method.[8] The dichloride (0·39 g.) was heated in ethanol (30 ml.) with brucine (0·32 g., 0·5 equiv.) at 60° for 6½ days, after which the chloride content of an aliquot part showed that 58% of the dichloride had reacted. The material was dissolved in ether, and brucine was removed by exhaustive extraction with aqueous sulphuric acid. The recovered material, which gave no colour reaction for brucine with concentrated nitric acid, had α_D −0·45° (0·25 g. in 5 ml. of $CHCl_3$; 1 dm. tube). Repeated washing with light petroleum gave a nearly pure specimen of the dichloride, m. p. 154°, α_D −1·67° (0·076 g. in 0·5 ml. of $CHCl_3$; 1 dm. tube). This corresponds to a specific rotation of *ca.* −11°. The recovery of optically active starting material indicates partial asymmetric decomposition of the dichloride, which must therefore be the racemic *trans*-9,10-dichloro-9,10-dihydrophenanthrene.

With ethanolic sodium hydroxide it gave 9-chlorophenanthrene, m. p. without further purification 47° (0·84 g. from 1 g.; 100% yield), identified also by its infrared spectrum. Its rate of dehydrochlorination with sodium ethoxide in ethanol was studied at 58·7°. The initial concentrations of organic compound and sodium ethoxide were 0·0340M and 0·1040M, respectively; 30 ml. portions were titrated with 0·01N-silver nitrate.

Time (min.)	0 *	140 *	15	30	45	61	74	∞
Titre (ml.)	1·02	1·88	4·65	8·34	11·43	14·38	16·46	103·0
k_2 (l. mole^{-1} min.$^{-1}$) †...	—	—	0·0228	0·0244	0·0236	0·0228	0·0220	—

* No NaOEt added. † These values correct an error in our preliminary communication.[5]

cis-9,10-*Dichloro*-9,10-*dihydrophenanthrene*.—This compound was present in the crude product obtained by treatment of phenanthrene with chlorine in a wide variety of solvents; it could be detected by its very great reactivity with alkali. Reaction in acetic acid gave material which was shaken with light petroleum (b. p. 40—60°); the *compound* began to separate and, when recrystallised from benzene–light petroleum, had m. p. 101° (Found: C, 67·9; H, 3·8; Cl, 28·5. $C_{14}H_{10}Cl_2$ requires C, 67·5; H, 4·0; Cl, 28·5%). Treatment of this material (0·16 g.) with brucine (0·12 g., 0·5 equiv.) in ethanol (50 ml.) for 19 hr. at room temperature (50% reaction) gave an organic product which within experimental error was optically inactive (0·143 g. in 1 ml. of $CHCl_3$ had a rotation of −0·005°; 1 dm. tube). So this isomer is the internally compensated, (*meso*-)*cis*-9,10-dichloro-9,10-dihydrophenanthrene. Like its isomer, it can be stored at −80° but decomposes slowly at room temperature. It gave 9-chlorophenanthrene in almost quantitative yield when heated or when treated with alcoholic alkali. Its rate of reaction with sodium ethoxide in ethanol was determined. Solutions of *cis*-9,10-dichloro-9,10-dihydrophenanthrene (initially $5{\cdot}06 \times 10^{-5}$M) and sodium ethoxide (initially 20×10^{-5}M) were mixed in a 1 cm. silica cell kept (thermostat) at 25°, and readings of the optical density were made at 3000 Å, at which wavelength *cis*-9,10-dichloro-9,10-dihydrophenanthrene has ε 1600, and 9-chlorophenanthrene has ε 13,960. The following are readings of optical density as a function of time, interpolated graphically (initial and final values are calculated from the observed spectra of the two compounds):

Time (min.)	0	2	4	7	13	20	∞
Optical density	0·081	0·205	0·299	0·397	0·498	0·557	0·707

Values of the integrated second-order velocity-coefficients calculated from these data fall from 560 l. mole^{-1} min.$^{-1}$ at the beginning of the reaction to about 540 l. mole^{-1} min.$^{-1}$ at 50% reaction. The main features of the infrared and ultraviolet spectra of these substances are recorded below.

Products of Reaction of Phenanthrene with Chlorine in Acetic Acid at 25°.—(i) *Hydrogen chloride*. After completion of the reaction, hydrogen chloride was determined in reaction mixtures by potentiometric titration with silver nitrate. End-points were stable and were not interfered

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[8] Cristol, Stermitz, and Ramey, *J. Amer. Chem. Soc.*, 1956, **74**, 4939.

with by other products. Great care was taken to avoid loss of hydrogen chloride by volatilisation when the sealed vessels were opened. Initial concentrations of chlorine were determined by control measurements. The following are the results:

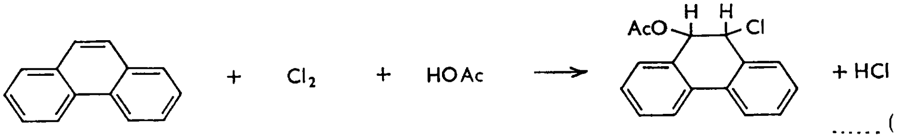
Init. ArH (M)	Init. Cl$_2$ (M)	Conditions	HCl produced/Cl$_2$ used up	Init. ArH (M)	Init. Cl$_2$ (M)	Conditions	HCl produced/Cl$_2$ used up
0·075	0·015	AcOH, 25°	0·59	0·10	0·01	AcOH, 35°	0·59
0·029	0·006	,, 25	0·57	0·10	0·01	,, 45	0·59
0·057	0·006	,, 25	0·58	0·07	0·04	,, 25; added LiCl, 0·02M	0·58
0·10	0·01	,, 15	0·58				

(ii) 9-*Chlorophenanthrene.* 9-Chlorophenanthrene was determined directly in the reaction mixture by the method of isotopic dilution. To a mixture which contained initially 4·50 millimoles of phenanthrene and in which, by titration, it was established that 0·416 millimole of ^{36}Cl-labelled chlorine had been consumed, inactive 9-chlorophenanthrene (16·68 millimoles) was added. The mixture was then worked up quickly at as low a temperature as possible to avoid decomposition of the dichloride adducts. The molar radioactivity of the diluted 9-chlorophenanthrene after recrystallisation to constant radioactivity showed that 0·1438 millimole of 9-chlorophenanthrene had been produced. On this basis, 0·345 mole of 9-chlorophenanthrene is formed from each mole of chlorine. Repetition gave 0·334 mole.

In a separate experiment, in which 0·414 millimole of ^{36}Cl-labelled chlorine were used up in reaction with a similar excess of phenanthrene, and the reaction mixture was diluted with 11·59 millimoles of inactive 9-chlorophenanthrene, the bulked diluted organic products were refluxed with an excess of ethanolic alkali for 6 hr. The recovered 9-chlorophenanthrene, now derived in part from the dichloride adducts, had after purification radioactivity corresponding with the formation of 0·3225 millimole (*i.e.*, of 0·78 mole from each mole of chlorine).

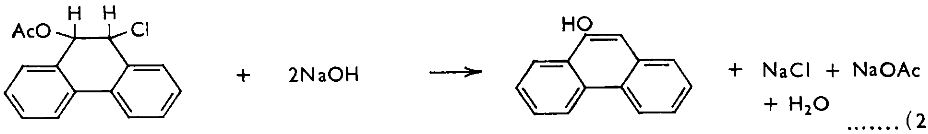
(iii) *Acetoxy-chloride adducts.* The crude product of reaction between chlorine and phenanthrene in acetic acid, isolated by ether extraction and carefully freed from acetic acid, contained oxygen [determined by direct analysis (by A. Bernhardt)] and had a strong infrared absorption band at 1745 cm.$^{-1}$ together with an even stronger band with a main component at 1221 cm.$^{-1}$ and shoulders at *ca.* 1235 and 1205 cm.$^{-1}$. None of these bands appeared in the spectra of the starting material or the other known products; all are characteristic of acetates,[9] and the group of bands in the region of 1220 cm.$^{-1}$ appears to be characteristic of acetates in which the acetoxyl group is not restricted sterically to a single conformation about the C–O bond.[9]

Acetoxy-chloride adducts can be formed by such a reaction as:



...... (1)

Treatment of such adducts with alkali should give acetic acid, hydrogen chloride, and phenanthrol, thus:



.... (2)

Accordingly, the organic product of the reaction of phenanthrene (5 millimoles) with chlorine (2·32 millimoles) in acetic acid (50 ml.) was isolated quantitatively, acetic acid was removed by washing the ether solution with aqueous sodium hydrogen carbonate, and 10 ml. were treated with 10 ml. of 0·0435M-potassium ethoxide in 96% ethanol under reflux for 3 hr. After reaction was complete, aliquot parts were titrated potentiometrically (*a*) with 0·0151N-barium hydroxide, after addition of a known excess of 0·02M-hydrogen chloride, in a current of nitrogen; and (*b*) with silver nitrate. Both these volumetric solutions were standardised against the

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[9] Jones and Herling, *J. Amer. Chem. Soc.*, 1956, **78**, 1152; Dauben, Hoerger, and Freeman, *ibid.*, 1952, **74**, 5206.

same standard 0·02M-hydrogen chloride. The results showed that the product liberated 1·62 millimoles (69·8%) of total acid (assumed to be a mixture of hydrogen chloride and acetic acid, as was consistent with the shape of the titration curve) and 1·31 millimoles (56·5%) of chloride ions. 9-Chlorophenanthrene does not liberate chloride under these conditions. From the difference between the results it can be estimated that 0·31 millimole of acetic acid was liberated from the product by alkali; and hence, if a monoacetoxy-monochloride adduct is the main material responsible for the liberation of acetic acid from the product, that 13·4 moles % of chlorine are used up in the reaction to form acetoxychlorodihydrophenanthrene.

The chloride content of the aqueous extract of the reaction mixture was determined by potentiometric titration of an aliquot part against silver nitrate and found to be equivalent to 1·35 millimoles (58·2%). The sum of this figure and the chloride liberated from the reaction product with alkali (1·31 + 1·35 = 2·66 millimoles) exceeds the total chloride (2·32 millimoles) by 0·34 millimole (14·7%). This value ought also be represent an estimate of the amount of acetoxy-chloride adduct calculated as acetoxychlorodihydrophenanthrene. The mean of the two estimates (14%) is used in the following discussion.

The acetoxy-chloride adducts are difficult to isolate in a pure state, as they, like the dichloride adducts, tend to decompose on such chromatographic columns as we have tried.

(iv) *Materials dehydrochlorinated by alkali.* The organic products were carefully freed from hydrogen chloride and acetic acid by washing them in ether solution with aqueous sodium hydrogen carbonate and with water. The residue contained (*a*) material which reacted completely with an excess of alcoholic sodium ethoxide in 10 min. at room temperature, and (*b*) material which reacted much more slowly with alcoholic sodium ethoxide but could be destroyed completely by boiling alcoholic sodium ethoxide in 3 hr. The ratio of rapidly reacting to slowly reacting material, determined by back-titration with acid to the end-point of Bromocresol Green–Methyl Red, was 3·9.

Infrared Spectra.—These were recorded for Nujol mulls by using a Grubb-Parsons double-beam spectrophotometer. Some of the results are tabulated.

Infrared absorption bands (cm.$^{-1}$) of phenanthrene and some of its derivatives (range, 650—1350 cm.$^{-1}$).

			9,10-Dichloro-9,10-dihydrophenanthrene	
Phenanthrene	9-Chloro-phenanthrene	9,10-Dichloro-phenanthrene	*cis-* (m. p. 100°)	*trans-* (m. p. 157°)
				660m
			699m	704w
713m	722s	719m	712w	717w,sh
				725m,sh
733s	744s	753m	730s	732s
	756s		740m	
810s			759s	766m
	846w		809m	774w
				790w
861m			840m	813w
871m	858w		870sh	855w
	879m		874m	
946m	935m		941w	
971w			951w	
1000w			973w	973w
1036w	1042w		1026w	1031w
1089w			1045w	
1138w	1143w		1053w	
1147w			1125w	1126w
1196w	1188w		1163w	
	1205w			1176w
1242m	1242w		1186m	1219w
1299m	1279w		1220m	1230w
	1292w		1287w	
			1305w	1312w

Ultraviolet Spectra.—These were determined by using a Unicam S.P. 500 spectrophotometer, 95% ethanol being used as solvent. The spectra of the 9,10-dichloro-9,10-dihydrophenanthrenes are similar in general features to the spectrum of 9,10-dihydrophenanthrene.[10] The

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[10] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

broad absorption band in the region 2700 Å is somewhat reduced in intensity (particularly for the *trans*-compound) and shifted to longer wavelengths. The subsidiary absorption in the region of 3000 Å is reduced in intensity (particularly for the *cis*-compound) and hence is not clearly resolved. No significant absorption was detected in the region 3250—3500 Å, where phenanthrene, 9-chlorophenanthrene, and related compounds have a marked series of weak bands.

Values of the extinction coefficients at maxima and minima according to our measurements are as follows:

9,10-Dihydrophenanthrene, $\varepsilon^{2350}_{\text{min.}} = 5000$; $\varepsilon^{2640}_{\text{max.}} = 19{,}300$; $\varepsilon^{2950}_{\text{min.}} = 4800$; $\varepsilon^{3000}_{\text{max.}} = 5050$.

cis-9,10-Dichloro-9,10-dihydrophenanthrene, $\varepsilon^{2450}_{\text{min.}} = 5200$; $\varepsilon^{2700}_{\text{max.}} = 16{,}600$.

trans-9,10-Dichloro-9,10-dihydrophenanthrene, $\varepsilon^{2500}_{\text{min.}} = 4350$; $\varepsilon^{2750}_{\text{max.}} = 12{,}850$.

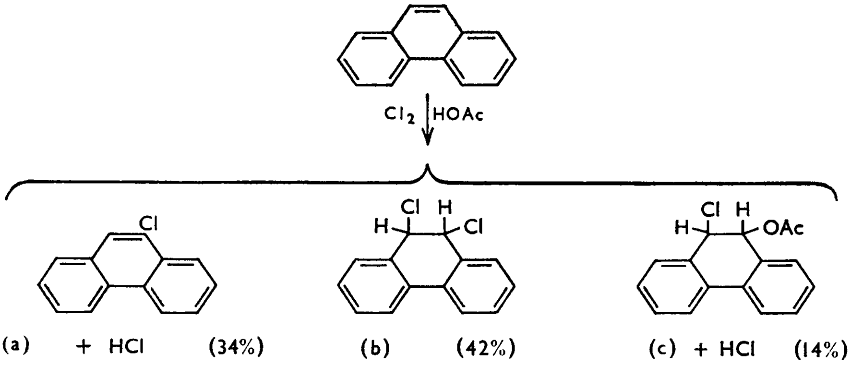
9-Chlorophenanthrene, $\varepsilon^{2300}_{\text{min.}} = 10{,}400$; $\varepsilon^{2550}_{\text{max.}} = 61{,}200$; $\varepsilon^{2850}_{\text{min.}} = 8850$; $\varepsilon^{2875}_{\text{max.}} = 11{,}200$; $\varepsilon^{2950}_{\text{min.}} = 7700$; $\varepsilon^{3000}_{\text{max.}} = 14{,}000$; $\varepsilon^{3170}_{\text{max.}} = 298$; $\varepsilon^{3270}_{\text{max.}} = 264$; $\varepsilon^{3330}_{\text{max.}} = 292$; $\varepsilon^{3430}_{\text{max.}} = 214$; $\varepsilon^{3500}_{\text{max.}} = 199$.

Rates of Reaction with Chlorine.—These were measured in acetic acid (m. p. 16·55°) essentially by conventional methods.[11] Precautions were taken to avoid loss of chlorine by volatility. For phenanthrene, the rate observed ($k_2 = 30 \pm 2$ l. mole^{-1} min.$^{-1}$ at 25° for *ca.* 0·004M-ArH and *ca.* 0·0015M-Cl_2) is in good agreement with that recorded by Mason,[12] but in poor agreement with the measurements recorded by Dewar and Mole.[13] We believe that the present value is substantially correct; and we obtained the same value within experimental error when the reaction mixture was illuminated and when the solutions were previously saturated and the vessels flushed either with nitrogen or with oxygen.

9-Chlorophenanthrene, as expected, reacted much more slowly ($k_2 = 0{\cdot}24$ l. mole^{-1} min.$^{-1}$ at 25° for *ca.* 0·04M-ArH, and *ca.* 0·01M-Cl_2). The isomeric 9,10-dichloro-9,10-dihydrophenanthrenes reacted still more slowly (*cis*-isomer, $k_2 = 0{\cdot}0015$ l. mole^{-1} min.$^{-1}$; *trans*-isomer, $k_2 = 0{\cdot}0009$ l. mole^{-1} min.$^{-1}$; both at 25°). These two reactions were followed for several days and *ca.* 10% reaction. So, in the time necessary for the reaction of phenanthrene and isolation of the product therefrom, these isomers do not decompose significantly to 9-chlorophenanthrene, which is more reactive than either by a factor of more than 100. This establishes that in the rapid reaction of phenanthrene in acetic acid no significant amount of 9-chlorophenanthrene is formed from either of the isomeric 9,10-dichloro-9,10-dihydrophenanthrenes.

Discussion

Detailed Course of the Reaction.—Cristol, Stermitz, and Ramey[8] found that acenaphthylene with chlorine in a non-polar solvent (where the *trans*-adduct was expected) gave *cis*-dichloroacenaphthene, whereas with benzene iodochloride (where the *cis*-adduct was expected) *trans*-dichloroacenaphthene was obtained. They proved unambiguously the structures of their adducts and commented on the mechanistic implications. The



(a) By isotopic dilution. (b) Total 9-chlorophenanthrene after treatment with alkali, 78%; hence from (a), by difference, 44%. From (HCl liberated) : (Cl_2 consumed), 42%. (c) From total acid and total chloride liberated by alkali from organic product.

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[11] Cf. de la Mare and Robertson, *J.*, 1943, 279.

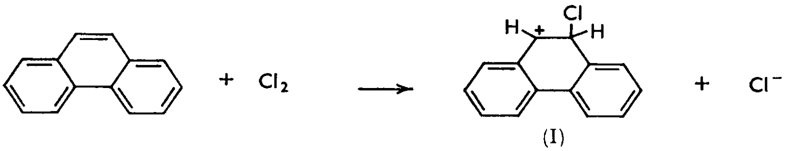
[12] Mason, *J.*, 1959, 1233.

[13] Dewar and Mole, *J.*, 1957, 342.

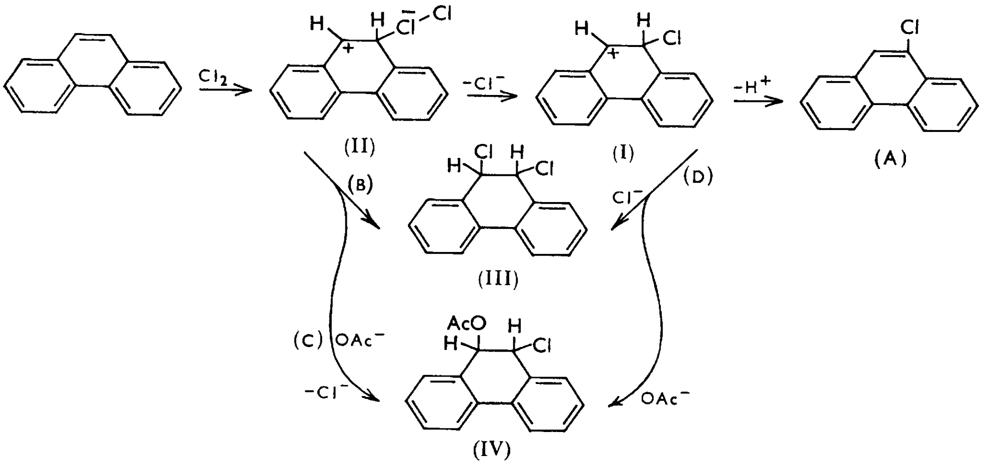
present results for phenanthrene are clearly related to Cristol, Stermitz, and Ramey's findings. For reaction with chlorine in acetic acid in the absence of electrolytes, our results can be summarised by the annexed scheme.

Neither *cis*- nor *trans*-9,10-dichloro-9,10-dihydrophenanthrene decomposes to give significant amounts of 9-chlorophenanthrene under the conditions of the reaction or the working up of the products. Formally, all the indicated products can be considered to be derived from a common carbonium ionic intermediate, (I).

Since, in the presence of added chloride ions, no less hydrogen chloride is produced than in its absence, a scheme involving only the carbonium ionic intermediate cannot adequately represent the reaction.

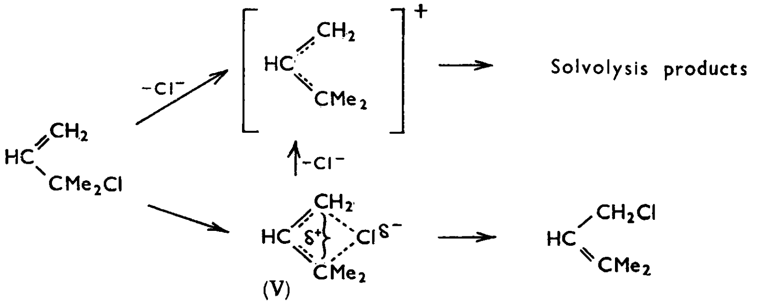


It is suggested, therefore, that the observations require a more elaborate scheme; the one which we favour is that involving reactions (A)—(D).



Route B is considered to give mainly the *cis*-isomer; it is suggested that it involves partial ionisation of chloride ion, through a transition state which in this solvent resembles an ion-pair, followed [as an alternative to loss of chloride ion giving the carbonium ion, (I)] by the internal capture of chloride ion to give mainly the *cis*-product.

Analogy may be drawn between the reaction of the neutral intermediate (II) to give alternatively the cation (I) or the adducts (III, IV), and the reaction of 1,1-dimethylallyl chloride to give products either of solvolysis or of rearrangement.[14]



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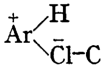
[14] Young, Winstein, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1958.

Those who believe that an ion-pair (V) is involved as an intermediate in the true sense (*i.e.*, a minimum which is actually reached by the reacting system in the potential energy surface) in the rearrangement and solvolysis of 1,1-dimethylallyl chloride should be as easily convinced that such an intermediate is the initial product of reaction of the neutral intermediate (II).

The cationic intermediate (I) would be expected by analogy with aliphatic systems[15] to give mainly the *trans*-isomer. In fact, the main products of addition are materials that react rapidly with alkali and must therefore have been formed by *cis*-addition (see below). Kinetic analysis of the reaction mixture is complicated by the fact that it seems that *cis*- and *trans*-isomers both of the dichloride adducts and of the acetoxy-chloride adducts are present. According to our analysis, the extreme assumption being made that all the acetoxy-chloride adduct might be *cis*-, not more than 11% of *trans*-dichloride, and hence not less than 31% of *cis*-dichloride, are produced in the reaction. Investigations leading to further details of the *cis-trans* ratio are in progress.

Route C, leading to acetoxy-chloride adducts, has not been elucidated in detail; it is possible that chloroacetates and dichlorides are in part produced also from the cationic intermediate (I; route D). It is intended to study in more detail the formation of acetoxy-chlorides as a function of the environment, but our analyses suggest that both *cis*- and *trans*-acetoxy-chlorides are formed.

P. W. Robertson and his co-workers[11,16] first emphasised that intermediates, $\overset{+}{\mathrm{Ar}}-\overset{-}{\mathrm{Hal}}-\mathrm{X}$, involving expanded octets of halogen, were helpful in rationalising kinetic features of the halogenation of aromatic compounds. In the course of the present series, and elsewhere,[17] the possible rôle of such intermediates in determining relative reactivities has been pointed out, and their probable importance in determining the relative effectiveness of reagents Cl–X has been discussed.[18] The present results suggest that the products and stereochemistry of the addition which accompanies substitutions are also in part determined by their intervention in the complicated sequences involved in reaction.

Elsewhere[17] we have stressed the structural analogy between the complexes,  $\overset{+}{\mathrm{Ar}}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\overset{-}{\mathrm{Cl}}-\mathrm{Cl}\end{smallmatrix}$ (*e.g.*, III), which we regard as concerned in these additions, and the trihalide ions ($\mathrm{Cl}-\overset{-}{\mathrm{Cl}}-\mathrm{Cl}$). In such complexes the central halogen bears 5 electron-pairs (hybridisation sp^3d), which are disposed at the corners of a trigonal bipyramid.[19] The favoured arrangement of the bonded groups in the trihalide ion places these so that the complex is linear. The alternative arrangements, with the Cl–Cl bond at right angles or at 120° to the Ar–Cl bond, illustrated in structure (VI) need, however, to be considered for the neutral complexes if our interpretation of *cis*-addition is correct. It seems likely that these particular electronic arrangements would not be very much less satisfactory than the linear alternative.

Orientation and Reactivity.—In the present investigation we have identified positively the conversion of 76% of the reacting chlorine into 9-chlorophenanthrene and 9,10-dichloro-9,10-dihydrophenanthrenes; and of 14% into material in which no chlorine remains in the organic nucleus after treatment of the product with alkali, *i.e.*, into acetoxy-chloride adducts. The amount of other nuclear-substituted phenanthrenes which can have been formed may be as large as 10%, though this figure is subject to the combined uncertainties of isotope-dilution and acetoxyl determination, and could possibly be in error by two or three units %. The conclusion that such isomers are present is consistent with theoretical calculations.

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[15] Lucas and Gould, *J. Amer. Chem. Soc.*, 1941, **63**, 2541.

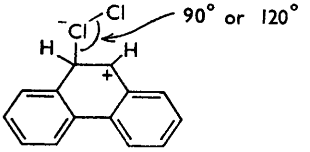
[16] Robertson, Dixon, Goodwin, McDonald, and Scaife, *J.*, 1949, 294; Robertson, *J.*, 1954, 1267.

[17] de la Mare, *J.*, 1949, 2871; "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publ., London, 1959, p. 219.

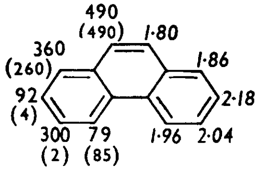
[18] de la Mare, Hilton, and Varma, *J.*, 1960, 4044.

[19] Gillespie and Nyholm, "Progress in Stereochemistry," ed. Klyne and de la Mare, Butterworths Scientific Publ., London, 1958, Vol. 2, p. 261.

For nitration, Dewar and his co-workers[20] have recorded the partial rate factors indicated in the formula (VII). In this, the italicised numbers are reactivity numbers,



(VI)



(VII)

N_x, which should, according to simple theory, be related to the partial rate factors through the equation:

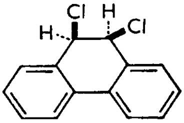
$$\log_{10} f_x = \text{Const.}\ (N_0 - N_x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where N_0 is the reactivity number (2·31) for benzene. If we assume that the proportionality constant can be obtained from the partial rate factor for the most reactive position, this theory predicts the partial rate factors for nitration given in parentheses; they accord only qualitatively with the experimentally observed values. It has been suggested[21] that the discrepancies arise in part because 1-, 4-, and 9-positions are partly sterically hindered for electrophilic substitution, but analysis of the non-bonded repulsions which might be concerned hardly supports this contention.[3]

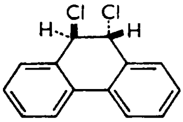
A similar analysis can be carried out in part for the chlorination of phenanthrene, by using the rate-ratio, phenanthrene : benzene = 1·02 × 10^6, established in the present series of investigations.[6] This value accords reasonably with an earlier estimate[3] from the best literature values. If the whole of the observed relative rate of reaction is divided between the various positions according to equation (3), then attack at the 9- and the 1-position should occur in the ratio 84 : 15; less than 1% of reaction should occur at the other nuclear positions. According to this calculation, therefore, up to 15% of 1-chlorophenanthrene might be formed in the chlorination. If the discrepancy between found and calculated values were in the same direction as for nitration, then still more of the 1-chloro-isomer should be present.

The dichloride adducts seem to be derived almost entirely from 9,10-addition, since the amount estimated by converting them into 9-chlorophenanthrene (44%) is the same within

(VIII)



(IX)



experimental error as that (42%) derived from the ratio of hydrogen chloride produced to chlorine consumed. It is possible, however, that the acetoxy-chloride adducts are not produced so exclusively by this mode of addition.

Chemistry of the 9,10-*Dichloro*-9,10-*dihydrophenanthrenes*.—Both isomers of this compound undergo elimination to give 9-chlorophenanthrene. The base-catalysed reaction of the *cis*-isomer (VIII) is undoubtedly a bimolecular (*E*2) elimination; it is faster than that for *cis*-dichloroacenaphthene or for any of the isomers of benzene hexachloride.[22] Examination of models shows that the dichloride (VIII) can exist in two equivalent nearly strainless conformations with about 20° between the planes of the aryl groups, in each of which one hydrogen is almost exactly conformationally *trans* to a chlorine atom, as is required for ready bimolecular elimination. This hydrogen atom is relatively accessible; it projects

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[20] Bavin and Dewar, *J.*, 1955, 4477; *J.*, 1956, 164; Dewar and Warford, *J.*, 1956, 3570.

[21] Dewar, Mole, and Warford, *J.*, 1956, 3581.

[22] Cristol, Hause, and Meek, *J. Amer. Chem. Soc.*, 1951, **73**, 674; Hughes, Ingold, and Pasternak, *J.*, 1953, 3832.

nearly at right angles to a plane drawn to approximate as nearly as possible to that of both rings.

The reactivity of the *trans*-isomer (IX) seems to be substantially less than that of β-benzene hexachloride,[22] which itself is less than that of *trans*-dichloroacenaphthene.[8] Two nearly strainless conformations are possible for the *trans*-isomer: in neither has either chlorine atom an available conformationally *trans*-hydrogen atom.

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