# **1134.** *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XVII.*[1] *Chlorination of 9,10-Dihydrophenanthrene.*

By P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas.

The rates and products of chlorination of 9,10-dihydrophenanthrene in acetic acid at 25° have been examined. They are discussed in relation to data on alkylbiphenyls; they indicate that the rate and orientation of substitution is changed by alteration of the angle between the planes of the benzene rings, and suggest that the transition state for chlorination of 9,10-dihydrophenanthrene is more nearly planar than that for chlorination of biphenyl.

In previous papers,[1,2] it has been shown that the rates and products of chlorination of substituted biphenyls can be altered by the presence of alkyl groups in the positions *ortho* to the Ar–Ar bond. The changes are of the type expected from the theory that the rate and orientation in such a system are determined by the availability of electrons supplied from one ring to the other; that this depends on the ease with which the two conjugated rings can approach planarity; and that a single 2-methyl group provides a substantial impediment to planarity.

Constraint of the angle between the two aryl groups can be imposed in another way, namely, by bridging the 2,2′-positions. In our preliminary communications [3,4] on these systems we reported that the rates of chlorination of biphenyl, 5-methyl-1,2:3,4-dibenzocyclohepta-1,3-diene, 9,10-dihydrophenanthrene, and fluorene support the view that the reactivity is related to the geometry imposed by the 2,2′-bridge. These results require supplementation by study of the orientation of chlorination, and we have since reported figures relating to the products of chlorination of fluorene.[5] In this paper we consider the chlorination of 9,10-dihydrophenanthrene, for which models show [6] strain to be minimised when the angle between the planes of the aryl groups is about 16°.

## Experimental

Some of the materials and methods have been described in earlier papers of this series. 9,10-Dihydrophenanthrene, m. p. 34°, had been prepared by catalytic reduction of phenanthrene and recrystallised from light petroleum or ethanol at low temperature.

For identification of the main products of chlorination of 9,10-dihydrophenanthrene it proved convenient to convert them into the corresponding chlorophenanthrenes. Three of these were already known. 1-Chlorophenanthrene was prepared by the sequence: $\gamma$-1-naphthylbutyric acid $\longrightarrow$ 1,2,3,4-tetrahydro-1-oxophenanthrene [7,8] $\longrightarrow$ oxime $\longrightarrow$ 1-aminophenanthrene [9] $\longrightarrow$ 1-chlorophenanthrene, m. p. 121° (lit.,[10] 120—120·5°) (Found: C, 79·0; H, 4·4; Cl, 16·8. Calc. for $C_{14}H_9Cl$: C, 79·1; H, 4·2; Cl, 16·7%). 3-Chlorophenanthrene was prepared by the sequence: 3-acetylphenanthrene [11] $\longrightarrow$ oxime $\longrightarrow$ 3-aminophenanthrene $\longrightarrow$ 3-chlorophenanthrene, m. p. 81° (lit.,[10] 80·5—81·5°) (Found: C, 79·4; H, 4·4; Cl, 16·4%). These compounds differed from the chlorophenanthrenes obtained by chlorination of 9,10-dihydrophenanthrene. Vapour-phase chromatography of the crude product, as described below, gave two main fractions. The larger was 2-*chloro*-9,10-*dihydrophenanthrene*; when crystallised from

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[1] Part XVI, de la Mare and Johnson, *J.*, 1963, 4076.

[2] de la Mare, Hall, Harris, Hassan, Johnson, and Klassen, *J.*, 1962, 3784.

[3] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.

[4] de la Mare, " Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths, London, 1958, p. 219.

[5] Beaven, de la Mare, Johnson, and Klassen, *J.*, 1962, 988.

[6] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854; Hall and Minhaj, *J.*, 1957, 4584.

[7] Haworth, *J.*, 1932, 1125.

[8] Bachmann and Wilds, *J. Amer. Chem. Soc.*, 1940, **62**, 2084.

[9] Langenbeck and Weissenborn, *Ber.*, 1939, **72**, 724.

[10] Bachmann and Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2097, 2194.

[11] Mosettig and Van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704.

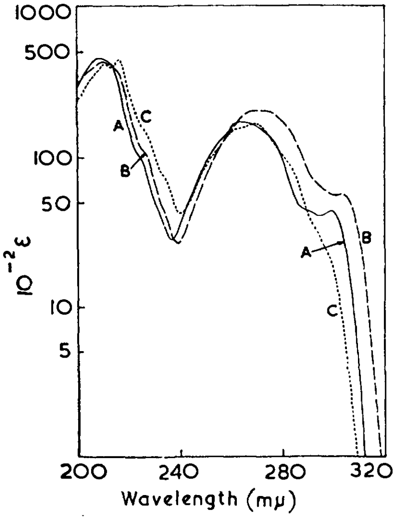
ethanol at −30°, it had m. p. 29—30° (Found: C, 78·1; H, 4·9; Cl, 16·9. $C_{14}H_{11}Cl$ requires C, 78·3; H, 5·2; Cl, 16·5%). Its ultraviolet spectrum in light petroleum (b. p. 100—120°) (see Figure) had $\lambda_{max.}$ 2095 (ε 42,500), $\lambda_{min.}$ 2390 (ε 2500), and $\lambda_{max.}$ 2710 Å (ε 21,100). Its infrared spectrum is recorded in Table 1, together with that of its isomer. On dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone it gave 2-chlorophenanthrene, m. p. 86—86·5° (lit.,[10] 85—85·5°).

TABLE 1.

Infrared absorption bands (cm.$^{-1}$; range 600—1380 cm.$^{-1}$) of 2- and 4-chloro-9,10-dihydrophenanthrene, and of 9,10-dihydrophenanthrene tetrachloride, in Nujol.

| 2-Chloro- | | 4-Chloro- | | Tetrachloride | |
|---|---|---|---|---|---|
| | 1007 m | 601 w | 1002 w | | |
| 644 w | 1022 m | 645 m | | 654 w | 1025 w |
| | 1030 w | | | 662 m | |
| | 1046 w | | 1048 w | 690 w | |
| 725 s | 1089 m | 722 s | 1086 w | 724 m | 1088 w |
| | 1107 m | 735 s | 1106 m | 734 m | 1106 w |
| | 1133 w | | 1140 m | 762 m | 1145 w |
| 765 s | | 778 s | 1151 w | 772 s | |
| 781 m | 1160 w | 790 m | | 792 m | |
| | | | 1173 m | 801 w | 1172 w |
| 822 s | 1189 m | 824 m | 1190 m | 829 m | 1196 w |
| 848 s | 1200 m | | 1200 m | 838 w | 1206 w |
| | | 867 w | | 870 w | 1225 w |
| 877 s | 1258 w | | 1243 w | 880 w | 1247 m |
| | 1267 w | 895 w | | | 1271 w |
| | 1299 w | 922 m | 1292 w | | 1298 w |
| 942 w | 1348 w | 943 w | 1350 w | 948 w | 1350 w |
| | | 963 w | | 968 w | |
| 986 w | | | | 984 w | |

The smaller fraction, an oil which we were unable to crystallise, was *4-chloro-*9,10-*dihydrophenanthrene* (Found: C, 78·4; H, 5·1; Cl, 16·6%). $\lambda_{max.}$ (see Figure) 2105 (ε 40,000), 2160 (ε 42,000), and 2695 Å (ε 17,000), $\lambda_{min.}$ 2400 Å (ε 4150). It underwent dehydrogenation much more slowly, and gave *4-chlorophenanthrene*, m. p. 58·5—59° (Found: C, 79·0; H, 4·0; Cl, 16·9%). This material was uniform on vapour-phase chromatography and, from its mode of formation and ultraviolet spectrum, is clearly a chlorophenanthrene. Its orientation, as well as that of the chloro-9,10-dihydrophenanthrene from which it was derived, is proved by the fact that it is different from the other four monochlorophenanthrenes. It is characterised and differentiated



Ultraviolet absorption spectra of (A) 9,10-dihydrophenanthrene and its (B) 2- and (C) 4-chloro-derivative.

———— 9,10-Dihydrophenanthrene.

— — — 2-Chloro-9,10-dihydrophenanthrene.

- - - - - 4-Chloro-9,10-dihydrophenanthrene.

Solvent : light petroleum (b. p. 100—120°).

from them especially by its melting point and its infrared spectrum. Spectroscopic data on 9-chlorophenanthrene have been recorded elsewhere,[12] and details relating to the other isomers will be published later.

Further information concerning the monochloro-9,10-dihydrophenanthrenes produced by chlorination of 9,10-dihydrophenanthrene was obtained by vapour-phase chromatography. The results were not significantly affected by treatment of the reaction product with alkali. Packed columns of the type referred to in earlier papers were used, with Apiezon M on Celite as stationary phase at 197°; the major components, 2- and 4-chloro-9,10-dihydrophenanthrene, were thus separated, as has already been indicated. Chromatography on a capillary column further resolved the monochloro-substitution products into four, as shown in Table 2.

TABLE 2.

Proportions, and retention volumes ($V_R$; 9,10-dihydrophenanthrene = 1) of monochloro-substitution products from 9,10-dihydrophenanthrene.

| Derivative | 4-Cl | 1-Cl * | 3-Cl * | 2-Cl |
|---|---|---|---|---|
| $V_R$ ................................. | 1·90 | 2·35 | 2·40 | 2·50 |
| Rel. amount (%) ................. | 20 | 1 | 3 | 60 |

* It is possible (though unlikely) that the assignments of the 1- and the 3-isomer should be reversed; see text.

The minor components must be 1- and 3-chloro-9,10-dihydrophenanthrene; and they have been assigned on the basis of their relative amounts, since substitution *ortho* to the methylene bridge should be disfavoured by the same steric and electronic effects which make the partial rate factor for *ortho*-substitution in toluene less than that for *para*-substitution.[13]

Vapour-phase chromatography of the products of chlorination, after alkali treatment, revealed also the presence of a series of dichloro-9,10-dihydrophenanthrenes, as judged from their retention volumes and ultraviolet spectra. Four or five were resolved on the larger columns; seven on the capillary column. Of these, three were prominent, and the remainder were minor components. The amounts varied with the conditions of chlorination, and with the proportions of chlorine to 9,10-dihydrophenanthrene used for the reaction.

There are two possible routes to dichlorodihydrophenanthrenes in these reactions: (*a*) by monosubstitution followed by further chlorination; and (*b*) by addition to form a polyhalide followed by elimination. Further evidence on this point was obtained by chromatographing the product of chlorination, a column of alumina or silica gel being used. The unchanged hydrocarbon, and any mono- and di-chloro-9,10-dihydrophenanthrenes produced directly in the chlorination or by decomposition of adducts during the isolation were eluted first with light petroleum. Elution with a mixture of light petroleum and ether (10%) then gave a fraction (*ca.* 3% yield, based on the hydrocarbon consumed) which on rechromatography gave material free from the substitution products. The material was crystalline; the best specimen had m. p. 115—120°. It was a 9,10-*dihydrophenanthrene tetrachloride* (Found: C, 52·1; H, 3·8; Cl, 44·2; $C_{14}H_{12}Cl_4$ required C, 52·2; H, 3·8; Cl, 44·0%). Its infrared spectrum contained characteristic bands at 662 and 690 cm.$^{-1}$; its ultraviolet spectrum in methanol had a broad band with $\lambda_{max.}$ 2690 Å ($\varepsilon$ *ca.* 13,000), with inflections at 2900 and 2990 Å, and $\lambda_{min.}$ 2395 Å ($\varepsilon$ *ca.* 6000). On treatment with alkali in ethanol under reflux, it liberated two equivalents of chloride (the molecular weight being assumed to be that of a dihydrophenanthrene tetrachloride). Its rate of alkaline dehydrochlorination (tabulated) was measured in 96% ethanol at 25°. A sample (0·0520 g. in 35 ml.) was mixed with 0·3265N-sodium ethoxide (10 ml.). At intervals samples (5 ml.) were removed for titration with 0·01059N-silver nitrate. The difference between

| | | | | | | | | Exp. | Calc. |
|---|---|---|---|---|---|---|---|---|---|
| Time (min.) ...... | 0·75 | 15 | 20 | 25 | 35 | 50 | 71·25 | ∞ | ∞ |
| Titre (ml.) ......... | 0·13 | 1·62 | 2·00 | 2·25 | 2·57 | 2·86 | 3·03 | 3·22 | 3·38 |
| $k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | 0·0127 | 0·0101 | 0·0111 | 0·0115 | 0·0105 | 0·0100 | 0·0091 | — | — |

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[12] de la Mare, Klassen, and Koenigsberger, *J.*, 1961, 5285.

[13] de la Mare and Ridd, " Aromatic Substitution—Nitration and Halogenation," Butterworths, London, 1959.

the experimental and the calculated values for the titre at infinity shows that the adduct was at least 95% pure. The rate coefficients are based on the experimental value.

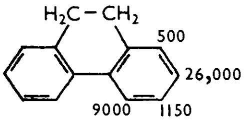
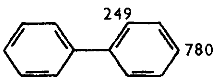
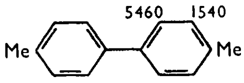
On vapour-phase chromatography the tetrachloride decomposed, to give a mixture of dichlorodihydrophenanthrenes (55%), chlorodihydrophenanthrenes (40%), and dihydrophenanthrene (*ca.* 3%). A little phenanthrene was also produced. The isomeric ratio in the monochlorodihydrophenanthrene fraction was rather similar to that obtained in the direct chlorination, though the amount of the 4-chloro-isomer was somewhat reduced. The chromatographic pattern of dichloro-substitution products was different from that obtained from alkaline decomposition of the adduct. From the latter reaction, only two dichlorodihydrophenanthrenes were formed in substantial amount, though traces of monochlorodihydrophenanthrenes and a very little dihydrophenanthrene were also formed.

*Acetoxy-chloride Adducts.*—By the determination of hydrogen chloride produced (*a*) by the reaction of a known amount of chlorine with an excess of 9,10-dihydrophenanthrene, and (*b*) by alkaline hydrolysis of the organic product formed in (*a*), the amount of acetoxy-chloride obtained by addition to 9,10-dihydrophenanthrene can be estimated; independent values were 2·6% and 1·4%, based on the chlorine consumed. We have been unable to confirm the presence of an acetoxy-chloride in the products by infrared analysis or by thin-layer chromatography. We consider therefore that not more than about 2% of the aromatic compound is consumed by formation of acetoxy-chloride adducts.

## DISCUSSION

(*a*) *Nuclear Substitution.*—There have been very few discussions of electrophilic substitution in 9,10-dihydrophenanthrene. Krueger and Mosettig [14] showed that nitration gives the 2-nitro-derivative as the major, and the 4-nitro-derivative as the minor, product. The present results for chlorination parallel these; we have shown also, however, that small amounts of the 1- and the 3-isomer can be detected in the product of monochlorination.

The partial rate factors derived from the rates [3] and orientation are shown in formula (I). They are derived with the usual assumption [2] that the relative proportions of isomers are not affected by diversion of part of the reacting material to products of addition. Values [2] for biphenyl (II) and 4,4′-dimethylbiphenyl (III) are given for comparison. In 9,10-dihydrophenanthrene the 2- and the 4-position are considerably more reactive than the corresponding positions in biphenyl. Still more significant is that the 4-position is more reactive than the 2-position in 4,4′-dimethylbiphenyl. Both these positions are activated by an *o*-aryl group and a *m*-methyl group. That substitution at the 4-position in 9,10-dihydrophenanthrene is not subjected to any unusual steric effect is shown by the fact that the ratio of 4- to 2-substitution (0·35) is very similar to the $\frac{1}{2}o : p$ ratio (0·32) for chlorination of biphenyl.

| Compound: |  |  |  |
|---|---|---|---|
| Rel. rate (PhH = 1) ...... | 12,200 | 426 | 4670 |
| | (I) | (II) | (III) |

Qualitatively, therefore, the partial rate factors for chlorination of 9,10-dihydrophenanthrene indicate that the ring is rather more activated than would be expected for a correspondingly substituted biphenyl. The amount of the extra activation is probably rather more than a factor of two, since electron-release to the *meta*-position by an $Ar{\cdot}CH_2{\cdot}CH_2$ group would probably be rather less than that from a methyl group. Activation of positions *ortho* and *para* to an aryl group is considered to be determined by conjugative electron-release from the aryl group; [4] so the results indicate that 9,10-dihydrophenanthrene can become a little more nearly planar in the transition state than 4,4′-dimethylbiphenyl, and by analogy biphenyl itself, is able to do. On this basis it must be accepted

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[14] Krueger and Mosettig, *J. Org. Chem.*, 1938, **3**, 340.

that there is a significant steric inhibition of conjugation in biphenyl and its non-*ortho*-substituted derivatives, revealing itself in a reduced rate of chlorination. In energy terms, it must be assessed at a value a little larger than that of the barrier to rotation about the aryl–aryl bond in 9,10-dihydrophenanthrene. This is not known experimentally, though the contribution to it from strains in the cyclic bridge has been estimated by Howlett.[15] Brown and Stock have recently reached a similar conclusion from study of the relative rates of electrophilic substitution in biphenyl and fluorene.[16]

The estimated partial rate factors for 1- and 3-chlorination are of the expected order of magnitude, being similar to those of the corresponding positions in the various alkyl biphenyls (cf. III). In principle, since these components are formed in amount similar to that of the adduct (see below), decomposition of the latter material could affect the isomeric composition derived from chromatography of the product. In fact, however, decomposition of the isolated adduct gives the 2-, 1-, and 3-chloro-isomers in very much the same ratio as is found in the direct substitution, and treatment of the crude reaction product with alkali before chromatography has very little effect on the estimated proportions of the isomers, so it appears that no significant error is introduced through this cause.

(*b*) *Addition Accompanying Substitution.*—As with biphenyl[17] and with fluorene,[5] reaction of 9,10-dihydrophenanthrene with chlorine in acetic acid gave some addition. The amount represented *ca.* 20% of the chlorine consumed.

The adduct isolated by chromatography of the product, was a rather unstable tetrachloride. It could be dehydrochlorinated by alkali, when it liberated two equivalents of hydrogen chloride. Its spectrum showed it to contain an unsaturated grouping conjugated with a benzene ring; the broad absorption band ($\varepsilon$ 13,100) is moved to longer wavelengths (2690 Å) than in phenylcyclohexene (2470 Å),[18] just as the corresponding absorption band in 9,10-dihydrophenanthrene occurs at a wavelength (2640 Å) longer than that of the corresponding band in biphenyl (2490 Å).[6] The course of its dehydrochlorination with alkali showed that it is essentially uniform in this respect, and that the second equivalent of hydrogen chloride is liberated at a rate similar to, or considerably faster than, that of the first.

These properties of the adduct, and its mode of decomposition on heating, are therefore in general very similar to those of the corresponding material isolated from biphenyl.[1] From the amount of hydrogen chloride produced relative to the amount of chlorine used up, it can be estimated that some 10% of the 9,10-dihydrophenanthrene gives adduct, calculated on the basis of a tetrachloride. The amount of adduct that we were able to isolate by chromatography did not exceed 3%; so the remainder must have been destroyed during the course of the isolation.

Some evidence was also produced for the presence of a little acetoxy-chloride adduct in the products of chlorination. There was, however, too little of this type of adduct for isolation.

(*c*) *Reaction Paths Adopted in Chlorination.*—The present results accord with the general picture used [2-5] to interpret the reactions of aromatic hydrocarbons with chlorine in acetic acid. The reactions appear to be heterolytic in character, since homolytic side-chain substitution is not detected even when aliphatic side-chains are present. Addition to the aromatic ring is rather common and is easily interpreted as proceeding by diversion of a carbonium-ionic intermediate, which is attacked by a nucleophile to give an adduct which may undergo further reaction with chlorine. In the case of biphenyl derivatives, a rather common result seems to be the formation of a tetrachloride, though acetoxy-chlorides are also formed.

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[15] Howlett, in Hall and Turner, *J.*, 1955, 1242.

[16] Brown and Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 1238, 1242.

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

[18] Carlin and Landerl, *J. Amer. Chem. Soc.*, 1953, **75**, 3969; Baddeley, Chadwick, and Taylor, *J.* 1956, 451.

The present results allow comparison of the behaviour of biphenyl and the alkylbiphenyls with those of fluorene and 9,10-dihydrophenanthrene. Experiments are in progress on hydrocarbons in which the bridging ring is still larger, and detailed discussion of the rate-comparisons is deferred until these can be reported.

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Chemistry Department, Bedford College,
Regent's Park, London N.W.1.
Medical Research Council Laboratories,
Holly Hill, London N.W.2.

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