Some Observations relating to Substituent Effects in Halogenation. Part VIII.[1] The Kinetics and Reactions of Indane, 9,10-Dihydroanthracene, and Tetralin with Chlorine Acetate in Aqueous Acetic Acid

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Rates of chlorination of 9.10-dihydroanthracene, indane, and tetralin with chlorine acetate and its protonated form in aqueous acetic acid at 25° have been examined and the product obtained determined by g.l.c. The partial rate factors have been calculated. The reactivity decreases in the order tetralin > 9.10-dihydroanthracene > indane. α-Aryl reactivities follow the same trend. The α : β reactivity ratios found for these compounds confirm earlier results found for nitration, bromination, and tritiation and which were explained by a combination of strain and hybridization effects. The α-aryl position in all these compounds show enhanced reactivity in the presence of catalytic amounts of mineral acid, this being particularly shown by the α-position in indane.

THE behaviour of reduced benzocycloalkenes in electrophilic substitution reactions has been examined with various reagents. Vaughan *et al.* have investigated the reactions of tetralin and indane with brominating and nitrating agents.[2] Nitration of tetralin and indane with nitric acid in acetic anhydride gave 74% α- and 26% β-nitro-isomer while nitration of indane gave 16% α- and 84% β-nitroindane. Bromination by bromine in aqueous acetic acid gave 61% α- and 39% β-bromotetralin whereas the isomeric bromoindanes were produced to the extent of 22% for the α- and 78% for the β-isomer. These results show that β-substitution predominates over α- in indane by comparison with tetralin and *o*-xylene. The observed orientation was explained by the greater stabilisation of the transition for β-substitution over that for the α-aryl position in indane. It was pointed out that in the Wheland intermediate for α-substitution the bond common to both rings has 2/3 double bond character whereas for β-substitution it has only 1/3 double bond character. For indane this will lead to greater strain in the non-aromatic ring. The transition state is thereby destabilised and the reactivity of the α-aryl position will be decreased thus leading to predominant substitution at

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[1] Part VII, preceding paper.

[2] J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1965, **21**, 1665.

the β-position. Tetralin is relatively strain free and thus the extent of α-substitution is higher than in indane.

Few studies are available of the substitution reactions of 9,10-dihydroanthracene. Most deal with formation of the 9,10-disubstituted products as intermediates in the preparation of 9,10-disubstituted anthracenes.[3,4] Kinetic studies of detritiation of the substrate have been carried out by Taylor *et al.*[5] who established the positional reactivities of the α- and β-positions.

Recently Bassindale *et al.*[6] studied the rates of protodesolylation of 1,2-dihydrobenzocyclobutene, indane, and tetralin. They established that while the α-position in 1,2-dihydrobenzocyclobutene has low reactivity, the β-position possesses normal reactivity by comparison with *o*-xylene. Also in indane the α-aryl position shows somewhat lower reactivity while the β-position shows enhanced reactivity as do the α- and β- positions in tetralin and they suggest that both the strain effect put forward by Vaughan *et al.*[2] and Taylor [5,7] and the hybridisation effect suggested by Streitweiser [8] operate to determine the reactivities at these positions.

In the present investigation the reactivity of indane, 9,10-dihydrophenanthracene, and tetralin towards chlorine acetate and its protonated forms has been determined by evaluation of the partial rate factors. The change in the reactivity of the electrophilic reagents (though they introduce the same substituent) might shed some light on the electronic or other factors governing the reactivities of these positions.

EXPERIMENTAL

Preparation and Purification of Materials.—Acetic acid was purified according to previous procedures adopted in earlier papers.[1] Indane had b.p. 176°, n_D^{25} 1.5381 (lit.,[9] 177., n_D^{25} 1.5381[10]). 9,10-Dihydroanthracene had m.p. 108.5° (lit.,[11] 108.5°). Tetralin was a commercial specimen purified by standard methods,[12] and had b.p. 207°, n_D^{17} 1.54529 (lit.,[13] b.p. 207.3°, n_D^{17} 1.54529). 4-Chloroindane was prepared from β-(*o*-chlorophenyl)propionyl chloride following ref. 6, b.p. 114—115° at 29 mmHg (lit.,[14] 60° at 2, 108—110° at 24 mmHg) (Found: C, 70.85; H, 5.8; Cl, 23.2. Calc. for C_9H_9Cl: C, 70.85; H. 5.9; Cl, 23.2%). 1-Chloro-9,10-dihydroanthracene was prepared by reduction of 1-chloroanthraquinone to the corresponding hydroxy-compound by means of aluminium isopropoxide in propan-2-ol. The material obtained after removal of the solvent was crystallised from ethanol and had m.p. 178° (lit.,[15] 178°). The product was further reduced by red phosphorus and hydriodic acid to the corresponding 1-chloro-9,10-dihydroanthracene, a pale yellow solid, m.p. 105.5°. The chlorotetralins were prepared from the corresponding tetralins by the Sandmeyer reaction.

α-Aminotetrahydronaphthalene.—Sodium metal (12 g, 3M) was added over 30 min into α-naphthylamine (15 g, 0.6M) in boiling amyl alcohol (170 ml). The mixture was allowed to cool, extracted with ether, dried ($CaCl_2$), filtered, and the solvent removed. Excess of concentrated hydrochloric acid was added and the hydrochloride so formed was washed several times with acetone, and neutralised with sodium hydroxide. The free amine which separated as a viscous oil was then extracted with ether, dried, converted into the hydrochloride, washed with acetone, and obtained as colourless *solid* (17 g, 90%) from dilute hydrochloric acid, m.p. 258° (Found: C, 65.35; H, 7.7; Cl, 19.25; N, 7.6. $C_{10}H_{14}ClN$ requires C, 65.4; H, 7.7; Cl, 19.3; N, 7.6%).

α-Arylchlorotetrahydronaphthalene.—The amine was diazotised by the normal procedure and was reacted with copper(I) chloride. The chloro-compound was obtained by steam distillation, washed with sulphuric acid (5N) to remove traces of the diazonium compound, then with sodium carbonate, and finally with water. The product was extracted with ether and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was eluted through alumina type H with light petroleum (b.p. 40—60°). α-Arylchlorotetrahydronaphthalene was obtained as a liquid, b.p. 71° at 0.3 mmHg, n_D^{20} 1.5034 (lit.,[16] 118° at 12 mmHg). The β-chloro-isomer, prepared in a similar manner from β-naphthylamine, had b.p. 72.8° at 1.4 mmHg. (lit.,[16] 118.5° at 12 mmHg).

Kinetic Measurements.—The rate of chlorination of the aromatics was followed iodometrically using standard procedures.[1] Table 1 gives an example of a typical kinetic run.

TABLE 1

Typical kinetic run for indan (0.0353M), ClOAc (0·01506M), and $AgClO_4$ (0.0300M) in 99% HOAc at 25°

Time (min)	0.00	1.90	8.60	12.20	20.10	22.80
Titre (ml)	14.9	13.75	10.60	9.30	7.10	6.50
k_2/l mol^{-1} min^{-1}		1.185	1.20	1.19	1.19	1.19

The rate coefficient for benzene under these conditions is $k_2 = 0.071$ l mol^{-1} min^{-1} (M. Hassan and A. S. Osman, *J. Chem. Soc.*, 1965, 2194).

Product Analysis.—Analyses of the products were carried out by g.l.c. The reaction mixtures were prepared under kinetic conditions and allowed to proceed to completion. They were then neutralised (NaOH) and extracted with ether. Solvent was removed and g.l.c. analysis was performed without further work-up. Authentic samples of the expected chloro-isomers were prepared and their retention times determined. The chromatogram for the reaction of 9,10-dihydroanthracene showed two chloro-products. One had the retention time for 1-chloro-9,10-dihydroanthracene. The other had that for the 2-chloro-isomer whose presence was assumed. Also, from the known retention time of α-chloroindane the β-isomer was determined in the same manner. The percentages of isomers

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[3] K. M. Mayer and K. Zahn, *Annalen*, 1913, **396**, 166.

[4] J. F. B. Lloyd and P. A. Ongley, *Tetrahedron*, 1965, **21**, 245.

[5] R. Taylor, G. J. Wright, and A. J. Holmes, *J. Chem. Soc.* (*B*), 1967, 780.

[6] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 12.

[7] R. Taylor, *Chimica*, 1968, **22**, 1.

[8] A. Streitwieser, jun., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

[9] W. Borsche and A. Pommer, *Ber.*, 1929, **54**, 102.

[10] S. Dev, *J. Indian Chem. Soc.*, 1953, **30**, 815.

[11] H. Weiland, *Ber.*, 1912, **45**, 492.

[12] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 3rd edn., p. 759.

[13] M. Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 644.

[14] L. F. Fieser and E. B. Hershber, *J. Amer. Chem. Soc.*, 1937, **59**, 394.

[15] S. Coffey and V. Bayd, *J. Chem. Soc.*, 1954, 2468.

[16] G. Schoeter, *Ber.*, 1938, **71**, 1040, 1044.

were determined by triangulation. The units employed were those used previously.[1]

DISCUSSION

The reactions of chlorine acetate with aromatic compounds in acetic acid take the kinetic form $-d[ArH]/dt = k_2[ArH][ClOAc]$. In the presence of catalytic amounts of mineral acid the kinetic form is consistent with the participation of protonated forms of the reagent.

Products.—Three general conclusions can be drawn from the quantitative studies of bromination and nitration of these compounds.[2] First, indane was shown to give a substantially greater proportion of β-substitution than *o*-xylene and tetralin, with *o*-xylene giving a product distribution which lies between those of indane and tetralin. Secondly, for bromination by molecular bromine in glacial and aqueous acetic acid, the extent of β-substitution increases (*i.e.* the α : β ratio decreases) as the medium is made more aqueous. Thirdly, the α : β ratio for substitution is greater for bromination by positive bromine than for bromination by molecular bromine. These results are confirmed by our present investigations for indane and 9,10-dihydroanthracene and are largely applicable to tetralin though in this case the ratios are not sufficiently well spread to allow any firm conclusions to be drawn.

TABLE 2

ArH	Partial rate factors	
	α-Aryl	β-Aryl
Tetralin		
ClOAc, 99%, 25°	543	306
ClOAc, $HClO_4$, 75% HOAc, 25°	996	600
ClOAc, 75% HOAc, 25°	850	438
Detritiation	3 750	4 000
Protodesilylation	88	67
9,10-Dihydroanthracene		
ClOAc, 99% HOAc, 25°	80	91
ClOAc, $HClO_4$, 75% HOAc, 25°	182	187
ClOAc, 75% HOAc, 25°	99	126
Detritiation	444	650
Indane		
ClOAc, 99% HOAc, 25°	11	40
ClOAc, 75% HOAc, 25°	10	38
ClOAc, $HClO_4$, 75%, 25°	43	66
Protodesilylation	29	78
Detritiation	1 000	4 200
Diphenylmethane		
ClOAc, 99% HOAc, 25°		
ClOAc, 75% HOAc, 25°	31	38
ClOAc, $HClO_4$, 75% HOAc, 25°	28	33
o-Xylene		
ClOAc, 99% HOAc, 25°	253	302
ClOAc, $HClO_4$, 75% HOAc	617	537
ClOAc, 75% HOAc	354	473
Protodesilylation	72	56
Detritiation	1 335	1 895

The relative rates and product compositions determine the partial rate factors for the various positions as shown in Table 2. The sequence of reactivity found, tetralin > *o*-xylene > 9,10-dihydroanthracene > indane, confirms the results for detritiation and protodesilylation. The activity at the α- and β-position in 9,10-dihydroanthracene is reduced by a factor of *ca.* 3 for the corresponding positions in *o*-xylene. The reason is thought to be due to the electron-withdrawing effect of the phenyl group rather than to steric factors since the phenyl substituent is held away from the ring at which substitution occurs. A similar relationship also holds in detritiation of the two substrates. In diphenylmethane[17] where both electronic and steric factors operate, its reactivity is reduced considerably by comparison with 9,10-dihydroanthracene and *o*-xylene.

The α : β reactivity is greatest in tetralin and least in indane. The greater α : β ratio for *o*-xylene over that for tetralin in protodesilylation must be due to steric acceleration in the reaction of the former compound. The high reactivity of the α-position in tetralin over 9,10-dihydroanthracene and indane is ascribed to the relatively strain-free conformation.

The α-aryl reactivity of these compounds is greater in reactions of the substrates with the protonated than with the molecular form of the reagent. The increase in α-aryl reactivity is particularly noticeable in indane where the α : β ratio increases from 0·27 for the molecular form of the reagent to 0.65 when mineral acid is present. This does not only reflect the change in the reagent, but also for indane a greater stabilisation of the transition state for α-substitution by comparison with that for its reaction with molecular chlorine acetate. Norman and Radda [18] in investigating the *ortho* : *para* ratio in electrophilic aromatic substitution have examined the Hammond postulate with reference to the structure of the transition state, that it resembles the reactants when these are of high reactivity and the Wheland intermediate when they are of low reactivity. The implications of this was that for reagents of low reactivity the conjugate interactions of the substituent are more effective at the *para*- than at the *ortho*-position and thus the *ortho* : *para* ratio is not expected to be high. When the reagents are of high reactivity, the transition states in these reactions should involve only minor deformations so that the relative reactivities of the *ortho*- and *para*-positions should be determined by the electron densities at these positions, and since the inductive effect operates more strongly at the *ortho*- than the *para*-position, then the *ortho*-position should exhibit higher reactivity than the *para*-position with the consequence that the *ortho* : *para* ratio should be higher than the previous case. All the substrates under examination exhibit higher α : β reactivity with the protonated forms but the extent to which it is shown by indane can only be explained by the lesser destabilisation of the transition state for α-substitution by comparison with its reaction with the less reactive molecular chlorine acetate. In the reaction of indane with the latter reagent the transition state is expected to resemble the Wheland intermediate in which the strain developed in the five-membered ring does not favour substitution in the α-aryl position, thus leading to a high β : α reactivity in indane.

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[17] M. Hassan and G. Yousif, *J. Chem. Soc.* (*B*), 1968, 459.
[18] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 1961, 3610.

The results for 9,10-dihydroanthracene and diphenylmethane reveal interesting features. Taylor *et al.*[5] found that the value of $\log_{10} f_o^{\mathrm{CH_2Ph}}/\log_{10} f_p^{\mathrm{CH_2Ph}}$ for detritiation of diphenylmethane (0.81) increases to 0.94 for the corresponding positions in the reaction of 9,10-dihydroanthracene. The increase was rationalised on the basis of a $-I$ effect associated with the phenyl substituent in diphenylmethane and also of steric hindrance in the *ortho*-position of the latter compound. In Table **3** we give further values of this ratio in chlorination by molecular and protonated forms of the reagent.

Table 3

Reaction conditions	Diphenylmethane $\log_{10} f_o/\log_{10} f_p$	9,10-Dihydroanthracene $\log_{10} f_o/\log_{10} f_p$
ClOAc, 99% HOAc, 25°	0.9928	0.9716
ClOAc, 75%, $HClO_4$, 25°	0.9535	0.9947

For reaction by molecular chlorine acetate the ratio is higher for diphenylmethane than for 9,10-dihydroanthracene, presumably due to the strain developed in the Wheland intermediate which should reduce the reactivity at the *ortho*-position (α-aryl position), in 9,10-dihydroanthracene, whereas in the reaction with the more reactive electrophile the $\log_{10} f_o/f_p$ ratio is greater for 9,10-dihydroanthracene than diphenylmethane since the transition state is expected to resemble the ground state more than the Wheland intermediate and hence the operation of the $-I$ effect of the phenyl substituent in diphenylmethane reduces the extent of *ortho*-substitution to a greater extent than does the phenyl group in 9,10-dihydroanthracene since it is common to both rings. The difference though small is significant and is presumably due largely to this effect. Differences in steric requirements are thought to be negligible since for the reactions of substituted diphenylalkanes de la Mare *et al.*[19] have pointed out the unusual activation of the 2-position in these compounds towards electrophilic reagents.

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[19] P. B. D. de la Mare, E. A. Johnson, and S. J. Lomas, *J. Chem. Soc.*, 1965, 6893.