537. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part X.*[1] *Products in the Chlorination of Biphenyl in Acetic Acid.*

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The products of reaction of biphenyl with chlorine in acetic acid have been examined, particularly by vapour-phase chromatography and isotopic dilution analysis. The $\frac{1}{2}o : p$ ratio is 0·3; very little, if any, 3-chlorobiphenyl is produced; and accompanying the substitution is an addition which consumes *ca.* 14% of the chlorine.

The phenyl group is inductively electron-withdrawing, but can also, when appropriately oriented, withdraw or release electrons conjugatively ($-I$, $\pm T$). Its response to the electronic requirements of a reaction-centre depends on the nature of the reaction, and hence it is sometimes said to have several σ-values, some of different sign.[2] Conjugative effects of substituents can, in principle, be transmitted through one ring of a biphenyl system to the adjoining ring,[3] but the quantitative importance of this effect is variable [4,5] and has not been examined very systematically.

Theoretical calculations [6] which relate reactivities of biphenyl with those of polycyclic aromatic hydrocarbons involve assumptions concerning the magnitude of the energy barrier restricting rotation about the Ar–Ar bond in biphenyl. Current opinions [7] concerning this quantity include values in the range 0—4 kcal. mole^{-1}, and a considerable effect on reaction velocity and on orientation is to be expected from steric inhibition of conjugation in 2-substituted biaryls.[8]

The rate of molecular chlorination in acetic acid depends much on structural effects, and particularly on conjugation.[9] It seemed useful, therefore, to extend our studies to biphenyl and its derivatives. This paper reports the commencement of such an investigation, including a side-reaction of addition (previously not generally recognised for such compounds in this solvent) whose importance is assessed; the more general considerations will be discussed in other papers.

Experimental

Materials and Methods.—Some of the materials and methods have been described in previous papers in this series. 2-Chlorobiphenyl, m. p. 33·5° (lit.,[10] 34°) was prepared from 2-aminobiphenyl by the Sandmeyer procedure. The following compounds were prepared from benzene and commercial specimens of the appropriate amines, by the Gomberg reaction: [11] 4-chlorobiphenyl, m. p. 77°; 3-chlorobiphenyl, b. p. 106—108°/*ca.* 0·1 mm., n_D^{25} 1·6175; 2,4-dichlorobiphenyl, n_D^{25} 1·6169 (Found: C, 64·4; H, 3·7; Cl, 31·5. Calc. for $C_{12}H_8Cl_2$: C, 64·6; H, 3·6; Cl, 31·8%); 2,5-dichlorobiphenyl, n_D^{25} 1·6154 (Found: C, 64·4; H, 3·7; Cl, 31·5%); 3,4-dichlorobiphenyl, n_D^{25} 1·6340 (Found: C, 64·6; H, 3·7; Cl, 31·5%). 3,5-Dichlorobiphenyl, prepared by dichlorination of 2-aminobiphenyl followed by deamination of the product,[12] had

[1] Part IX, de la Mare, Hilton, and Varma, *J.*, 1960, 4044.
[2] Berliner and Liu, *J. Amer. Chem. Soc.*, 1953, **75**, 2417.
[3] Cf. Berliner and Blommers, *J. Amer. Chem. Soc.*, 1951, **73**, 2479.
[4] de la Mare and Ridd, "Aromatic Substitution—Nitration and Halogenation," Butterworths, London, 1959, pp. 157 ff.
[5] de la Mare and Robertson, *J.*, 1948, 100.
[6] Dewar, *J.*, 1957, 342; R. D. Brown, *J.*, 1959, 2224, 2232.
[7] Adrian, *J. Chem. Phys.*, 1958, **28**, 608; Howlett, *J.*, 1960, 1055; H. C. Brown, "Steric Effects in Conjugated Systems" (ed. Gray), Butterworths, London, 1958, p. 104; Coulson, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths, London, 1959, p. 57.
[8] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.
[9] Ref. 4, pp. 131 ff.
[10] Cf. Elks, Haworth, and Hey, *J.*, 1940, 1284; Augood, Hey, and Williams, *J.*, 1953, 44.
[11] Cf. Bachmann and Hoffman, "Organic Reactions," Vol. II, Wiley, New York, 1944, p. 224.
[12] Scarborough and Waters, *J.*, 1927, 89.

n_D^{25} 1·6257 (Found: C, 64·5; H, 3·8; Cl, 31·6%). They were purified by chromatography on silica gel, light petroleum (b. p. 40—60°) being used for elution. Vapour-phase chromatography showed them to be uniform and therefore almost certainly of high purity.

The infrared spectra are recorded in the Table. They were determined with a Grubb–Parsons double-beam spectrophotometer, solids being in Nujol mull, liquids as films between rock-salt plates. In our experience, small amounts (less than 5%) of 3-chlorobiphenyl were difficult to detect in admixture with the other isomers, especially when biphenyl also was present.

4-Chloro-4′-nitrobiphenyl was prepared by treating 4-chlorobiphenyl (4·2 g.) in acetic acid (10 ml.) with nitric acid (*d* 1·5; 4·2 ml.). The mixture was boiled under reflux for 2 hr. and then poured on ice. The solid was passed in benzene through a column of alumina. Elution and removal of the solvent gave a solid which on recrystallisation from ethanol had m. p. 144°, unchanged on further repeated crystallisation (Found: C, 61·6; H, 3·8; Cl, 15·6; N, 5·8. Calc. for $C_{12}H_8ClNO_2$: C, 61·6; H, 3·4; Cl, 15·2; N, 6·0%). Oxidation with chromic oxide in 75% acetic acid gave *p*-nitrobenzoic acid, m. p. and mixed m. p. 241°. The m. p. (144°) which we now record for 4-chloro-4′-nitrobiphenyl accords with that (143°) given by Angeletti,[13] who prepared the compound from 4-amino-4′-nitrobiphenyl by the Sandmeyer procedure; we did not succeed in attaining a m. p. as high as that (157°) given by Le Fèvre and Turner[14] for material obtained by catalysed chlorination of 4-nitrobiphenyl.

The dinitration of 4-chlorobiphenyl does not seem to have been described previously. We heated 4-chlorobiphenyl (4 g.) with sulphuric acid (3 ml.; *d* 1·89) and nitric acid (3 ml.; *d* 1·42) on a steam-bath for 1 hr. The product was poured on ice and washed with water. The organic product was treated with ether. The insoluble 4-chlorodinitrobiphenyl, recrystallised from ethanol, had m. p. 188—189° (Found: C, 51·6; H, 2·7; Cl, 13·1; N, 10·0. $C_{12}H_7ClN_2O_4$ requires C, 51·7; H, 2·5; Cl, 12·7; N, 10·1%). The ether-soluble fraction was also recrystallised from ethanol; it was another 4-chlorodinitrobiphenyl, m. p. 142—143° (Found: C, 51·8; H, 2·6; Cl, 12·6; N, 9·4%). One of these compounds should be 4-chloro-2,4′-dinitrobiphenyl obtained by nitration of the 4-chloro-4′-nitrobiphenyl formed first. Since this, by analogy with the behaviour of the dihalogenobiphenyls,[15] is unlikely to give much of the product of 3-nitration, it seems probable that the other isomer that we isolated is 4-chloro-2,2′- or -3,2′-dinitrobiphenyl, obtained through 4-chloro-2′-nitrobiphenyl; this compound, by analogy with the behaviour of 4,4′-dihalogeno-2-nitrobiphenyls,[15] might give a mixture of 3- and 2-nitro-derivatives.

The infrared spectra are tabulated.

Analyses by Isotopic Dilution.—(a) 4-*Chlorobiphenyl.* (i) Biphenyl (0·1637 mole) was allowed to react completely with ^{36}Cl-labelled chlorine (0·0573 mole) in acetic acid at 25° in the dark. To a portion of the mixture was added a known weight of 4-chlorobiphenyl. The diluted products were then isolated, and oxidised with aqueous potassium permanganate. *p*-Chlorobenzoic acid was repeatedly crystallised to constant m. p. (237—238°) and radioactivity. The molar activity, compared with that of the original chlorine (converted into lithium chloride for radioactive counting) gave the result that, of the chlorine undergoing reaction, 46·6 moles % had reacted to give 4-chlorobiphenyl by substitution.

(ii) In a similar experiment in which 0·261 mole of biphenyl had reacted with 0·0312 mole of chlorine, 4-chlorobiphenyl was isolated directly from the diluted mixture; the radioactivity of this indicated that the reaction gives 46·2 moles %. A further sample was nitrated, as described above; the 4-chloro-4′-nitrobiphenyl, m. p. 144°, had a radioactivity unchanged on repeated crystallisation which corresponded with the formation of 46·6 moles % of 4-chlorobiphenyl.

(b) 2-*Chlorobiphenyl.* (i) An attempt to determine the percentage of this isomer by oxidising the mixture after dilution with synthetic 2-chlorobiphenyl gave too high a value (53%). We attribute this to the presence of materials other than 2-chlorobiphenyl which are oxidised to *o*-chlorobenzoic acid. The following method gave a more reliable value.

(ii) The organic product was recovered from the diluted mixture and fractionally distilled *in vacuo*; biphenyl was removed at 115—116°/5 mm.; the remainder distilled at 108°/2 mm. The last fraction, crystallised from alcohol, had m. p. 33·5°, and its radioactivity, unchanged

[13] Angeletti, *Giorn. Farm. Chim.*, 1926, **75**, 262; *Chem. Zentr.*, 1926, II, 3045.
[14] Le Fèvre and Turner, *J.*, 1928, 253.
[15] Shaw and Turner, *J.*, 1932, 285; Marler and Turner, *J.*, 1931, 1359; 1937, 266.

Infrared spectra (cm.$^{-1}$; range 650—1600) of some chlorobiphenyls.

Chloro-substituent(s)								
2-	3-	4-	2,4-	2,5-	3,4-	3,5-	2,2'-	4,4'-
679m	683m				683sh	680sh	662m	
696s	694s	693s	695s	695s	693s	692s	695m	699m
721w			714w				719m	
746s							730m	720m
757sh	752s	756s	760s	763s	765s	766s	752s	810s
767m								
	789s		809s	810s	818s	798s		
		829s	818sh					
	879s		865m	880m	879m	852s	855w	846m
913w						871m		
942w						908w	943w	
						970w	978w	998m
1010m	1001m	1008m	1005m	1013m			1000m	
1036s	1020m		1032m	1032s	1024s		1021m	1015m
	1047s		1070m	1073w	1043w	1060m	1029m	
1076s	1082s				1075w	1073w	1052s	
	1099s	1092s	1099s	1098s		1092m	1079m	1082m
1128m				1131m	1129s	1118m	1122m	1096w
							1153w	1163w
	1258w			1241w	1250w	1278m	1235w	
					1285w		1255w	1290w
	1282w		1370m		1370m	1376w	1370s *	1370s *
	1412s	1406w	1439m	1417m	1431sh	1406m	1418s	
	1470sh		1460s	1438m	1456s	1428m	1447s *	1447s *
				1450s		1448w		
	1481s		1543m	1551w	1547w	1492m		
1508w	1571s		1583m	1586w	1587w	1552s	1555w	
	1600s		1600w			1583s		

* Nujol peaks.

on recrystallisation, corresponded to presence of 29·5% of 2-chlorobiphenyl in the product. A rather less pure fraction was nitrated as recommended by Mascarelli and Gatti.[16] There was obtained 2-chloro-4',5-dinitrobiphenyl, m. p. 159—160°, with a radioactivity which corresponded to 29·8% of 2-chlorobiphenyl in the original mixture (Found: C, 52·3; H, 2·9; Cl, 12·7; N, 10·0. Calc. for $C_{12}H_7ClN_2O_4$: C, 51·7; H, 2·5; Cl, 12·7; N, 10·1%). The $\frac{1}{2}o$: *p*-ratio from these experiments is therefore 0·32.

(c) *3-Chlorobiphenyl.* An attempt was made to estimate this isomer by isotopic dilution. The diluted mixture should have contained 0·66 g. of radioactive chlorobiphenyl together with 10·70 g. of added inactive 3-chlorobiphenyl. The mixture was nitrated with nitric and sulphuric acid; there was obtained a tetranitro-derivative, m. p. 127°, the specific activity of which corresponded to 12·5% of 3-chlorobiphenyl in the product. This value is far too high. It seems probable that exchange of radio-chlorine between the radioactive impurities and the nitrated 3-chlorobiphenyl occurs during the rather drastic conditions of nitration.

(d) *Chlorobenzene.* To an aliquot part of a mixture similar to those described above, chlorobenzene was added. The organic product was recovered and fractionally distilled. The recovered chlorobenzene had negligible radioactivity; on this basis, not more than 0·01% of chlorobenzene could have been formed in the reaction.

Analysis by Vapour-phase Chromatography.—The apparatus was similar to that employed previously,[17] and is described in more detail elsewhere.[18] Quantitative estimates were made on a basis of peak areas, corrected for molecular-weight difference where necessary. Apiezon L or M was used as a stationary phase at 197° for most of the work, but checks of minor components were carried out with other, more polar, stationary phases; in particular, the absence of a significant amount of 3-chlorobiphenyl was confirmed by using a nitrated 2-dodecylnaphthalene as stationary phase, on which the 3- and the 4-isomer are better separated.

With biphenyl in 10-fold excess over chlorine, the ratio 4-chlorobiphenyl : 2-chlorobiphenyl

[16] Mascarelli and Gatti, *Gazzetta*, 1933, **63**, 654; cf. Case, *J. Amer. Chem. Soc.*, 1943, **65**, 2137.
[17] (*a*) Beaven, James, and Johnson, *Nature*, 1957, **179**, 490; (*b*) Johnson, " Steric Effects in Conjugated Systems " (ed. Gray), Butterworths, London, 1958, p. 174.
[18] Johnson, Childs, and Beaven, *J. Chromatog.*, 1960, **4**, 429.

in the product was 62 : 38 ($\frac{1}{2}o : p = 0{\cdot}31$). Only traces of other materials were detected. Similar results were obtained when a smaller excess of biphenyl was used. Biphenyl (0·19 mole) was allowed to react with chlorine (0·38 mole). The reaction was stopped when 0·08 mole of chlorine remained; the major products and their relative proportions were then as follows: 2-chlorobiphenyl (20 parts); 4-chlorobiphenyl (19 parts); 2,4′-dichlorobiphenyl (5 parts); * and 4,4′-dichlorobiphenyl (9 parts). On Apiezon M at 197° the retention volumes of the monochlorobiphenyls, relative to biphenyl, were: 2-, 1·50; 3-, 2·30; 4-, 2·40. Those of the dichlorobiphenyls are as follows:

Dichlorobiphenyl	2,2′	4,4′	2,4′	2,4	2,5	3,4	3,5
Retention volume	2·25	5·80	3·65	3·25	3·15	5·50	4·70

These agree well with estimated values.[17b]

Production of Hydrogen Chloride.—To a solution of aromatic compound at 25° in acetic acid in the dark was added a standard solution of chlorine. The mixture was set aside for more than twenty reaction half-lives. A rubber tube was then fitted round the neck of the flask and filled with water. The stopper was then carefully freed so that water filled the dead-space in the flask but no hydrogen chloride escaped. The whole solution was then added to water and titrated potentiometrically with silver nitrate. Anisole gave 1·00 mole of chloride per mole of chlorine consumed. Biphenyl (0·029, 0·057, 0·075, 0·100 mole) and chlorine (respectively 0·006, 0·006, 0·015, 0·020 mole) gave respectively 0·832, 0·823, 0·824, and 0·828 (mean 0·827) mole of chloride per mole of chlorine used up.

Possible Formation of Acetoxy-chloride Adducts.—Direct oxygen analysis of the organic product isolated from one of the above experiments showed that very little material (" acetoxy-chloride adduct ") had been formed by addition of chlorine acetate (*e.g.*, by successive attachment of Cl^+ and OAc^-) to the aromatic nucleus. A separate test was carried out by refluxing the organic product, which had been carefully freed from acetic acid, with excess of sodium ethoxide. The solution was made just acid with 0·1N-sulphuric acid. Back-titration of an aliquot with 0·05N-sodium hydroxide to the end-point of Bromocresol Green–Methyl Red required 0·07 ml. of alkali. Back-titration to the phenolphthalein end-point of a second aliquot part which had been refluxed for 10 min. to remove dissolved carbon dioxide required 0·15 ml. of alkali. A control experiment in which β-hexachlorocyclohexane was used gave no significant difference between the titration to the two indicators, so it is concluded that the difference observed for the chlorinated product is experimentally significant and represents a titration of acetic acid; it corresponds with the production of *ca.* 2% of adduct, calculated as acetoxytrichlorotetrahydrobiphenyl, as a percentage of the chlorine used.

The crude chlorination product from biphenyl (30 g.) and chlorine (14 g.) in acetic acid was divided into three fractions by crystallisation from light petroleum. The most soluble fraction was dissolved in light petroleum and chromatographed on silica gel. 4-Chlorobiphenyl, 2-chlorobiphenyl, and biphenyl were eluted in that order with light petroleum. When these had been removed, the residue was eluted with ether. After the solvent had been removed, an oil (0·5 g., *ca.* 12% of the chlorinated material) was left. Several specimens of such material were rechromatographed; the product had the properties of a tetrachlorotetrahydrobiphenyl, as is shown by the following properties. Heating under reflux with an excess of sodium ethoxide gave 1·99 moles of hydrogen chloride per mole of adduct, calculated as $C_{12}H_{10}Cl_4$. Solvolysis in boiling 50% ethanol gave 0·78 mol. of acid after 9 hr., and 0·83 mol. after 18 hr. The ultraviolet absorption spectrum had a broad band with a maximum at 2500 Å (ε 9670, calc. as $C_{12}H_{10}Cl_4$) and a minimum at 2280 Å (ε 5410). The infrared spectrum had peaks (in the 650—1000 cm.$^{-1}$ region) at 954m, 917m, 868m, 821m, 773s, 757sh, 693s cm.$^{-1}$ (Found: C, 48·5; H, 3·4; Cl, 47·6. Calc. for $C_{12}H_{10}Cl_4$: C, 48·6; H, 3·4; Cl, 48·0%). Its rate coefficient for chlorination at 25° in acetic acid was $k_2 = 0{\cdot}007$ l. mole^{-1} min.$^{-1}$, about one sixth of that of biphenyl.

The product from treatment of the adduct with alkali was recovered (Found: C, 64·2; H, 3·8. Calc. for $C_{12}H_8Cl_2$: C, 64·6; H, 3·7%). It had infrared absorption bands at 875w, 854m, 820m, 811w, 799m, 757s, 693s, 684sh, s cm.$^{-1}$, and therefore appeared to be a mixture of 3,5- and 3,4-dichlorobiphenyl. This was confirmed by vapour-phase chromatography,

* This compound must be one of the major products of dichlorination of biphenyl; so we regard its identity as established by the vapour-phase chromatogram.

which showed that it contained dichlorobiphenyls in the following proportions: 3,5-, 59%; 3,4-, 33%; 2,4-, 6%; 2,5-, 2%. The last two isomers were separable only on a capillary column. There was also *ca.* 2% of material, the retention volume of which was consistent with its being a trichlorobiphenyl.

Neither the tetrachloride adduct nor more than a trace of dichlorobiphenyls was detected in the vapour-phase chromatograms of the products of chlorination of biphenyl with a deficiency of chlorine. The tetrachloride must, therefore, have a relatively high retention volume, and is not decomposed rapidly in the column. When, however, the crude product was distilled at ordinary pressure, the distillate contained increased amounts of 2,4(or 2,5)- and 3,4-dichlorobiphenyl; no significant amount of the 3,5-isomer was detected. Thermal decomposition of the tetrachloro-adduct must, therefore, give dichlorobiphenyls in proportions significantly different from those obtained by dehydrochlorination with alkali. This is not unexpected in view of the considerable difference in temperature and mechanism between the two reactions.

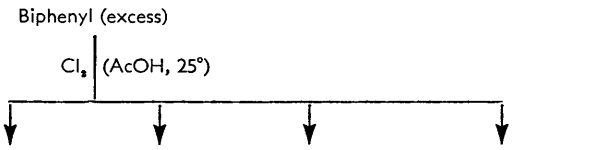
Discussion

The only product analysis previously recorded for the chlorination of biphenyl is that given by Jenkins, McCullough, and Booth [19] for chlorination of molten biphenyl at 90° with iron as a catalyst. The product was fractionally distilled; 36% of pure 2- and 29% of pure 4-chlorobiphenyl were isolated, and with reasonable assumptions concerning the composition of intermediate fractions, it can be estimated that there were formed 51% of 2-, 38% of 4-, and 12% of di- and poly-chlorobiphenyl ($\frac{1}{2}o : p$ 0·65—0·7).

In the present work, at a lower temperature, in acetic acid as solvent, the amount of *para*-substitution is about the same, but considerably less *ortho*-chlorobiphenyl is produced ($\frac{1}{2}o : p$ 0·31). This result has been confirmed by two independent methods of analysis, and there seems no reason to doubt its correctness under our experimental conditions.

We have been unable to detect 3-chlorobiphenyl in our products. Vapour-phase chromatography has been shown to detect easily the presence of 1% of this compound in a mixture with its isomers, so we feel confident that much less than this amount is present. This result is consistent with theoretical predictions based on the additivity principle. For, as has been shown elsewhere,[20] the 3-position in 4-acetamidobiphenyl is less reactive than the 2-position in acetanilide by a factor of 0·7; so, if this result can be carried over to the unsubstituted compound, the partial rate factor for *meta*-substitution in biphenyl is 0·7. From this and the total rate (422) of substitution relative to benzene,[8] the percentage of *meta*-substitution in biphenyl should be less than 0·06%.

The combined results for the analysis of reaction products by isotopic dilution, by vapour-phase chromatography, and by determination of hydrogen chloride liberated, and of the acetoxy-content of the isolated material, are summarised in the annexed chart.



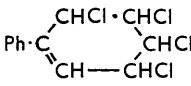
Cl_2 consumed (moles %)	30	46·5	17·5	*ca.* 2
Biphenyl consumed (moles %)	34	54	9	*ca.* 1

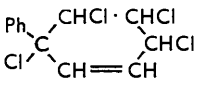
Only small traces of other materials were detected in the vapour-phase chromatograms, and disubstitution by chlorine is small when biphenyl is present in the excess used in these experiments.

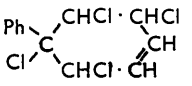
[19] Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31.
[20] de la Mare and Hassan, *J.*, 1958, 1519.

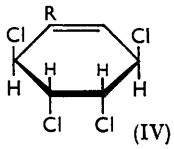
We have thus accounted in these experiments for about 96% of the total chlorine used; on a molar basis ~77% of the chlorine, and ~88% of the biphenyl, give products of substitution.

Of the chlorine consumed, ~17·5% gives an adduct, the major portion of which is a product in which two chlorine molecules have added to one ring of biphenyl. If stereoisomerism is neglected, the possible tetrachlorides are (I—III). Compounds (II) and


(I)


(II)


(III)


(IV)

(III) are probably at most minor components; for these materials, in which the double bond is not conjugated with the phenyl group, would not be expected to have intense absorption in the region of 2500 Å. 1-Phenylcyclohexene,[21] on the other hand, has $\varepsilon_{max.}$ 11,500 at 2470 Å, $\varepsilon_{min.}$ 4500 at 2250 Å, and the adduct has similar absorption ($\varepsilon_{max.}$ 9670 at 2500 Å; $\varepsilon_{min.}$ 5410 at 2280 Å).

The structure of the adduct can be further elucidated by consideration of the products obtained on reaction with alkali. Of the five known isomers of tetrachlorocyclohexene,[22] only one gives with alkali very little *p*-dichlorobenzene. This is the relatively unreactive α-isomer (IV; R = H). It seems likely that the phenyl group in the adduct would, if anything, favour the formation of a product containing *p*-chloro-substituents; so, since very little of this material (2,5-dichlorobiphenyl, 2%) was formed in the dehydrochlorination, we consider that structure (IV; R = Ph) represents the bulk of the adduct.

The rate of reaction of the adduct with alkali was also measured, and supports this view. For 0·00945M-$ArHCl_4$ and 0·0384M-sodium hydroxide in 80% ethanol at 30°, the plot of percentage reaction against time proceeded smoothly from the calculated initial titre to a value within 4% of the calculated infinity value. The rate-coefficient showed no significant change during the reaction; the second-order velocity coefficients, calculated by using the formula [23]

$$k_2 = \frac{2{\cdot}303}{t(B_0 - x)} \log_{10} \frac{x(B_0 - x)}{B_0(x_\infty - x)}$$

(where B_0 is the concentration of alkali at t_0, and x is the concentration of chloride liberated at time t), were 0·021 l. mole^{-1} sec.$^{-1}$ at 25% reaction and 0·024 l. mole^{-1} sec.$^{-1}$ at 80% reaction. So the reaction appears to characterise a single substance reacting with alkali to liberate the first chloride ion slowly and the second very rapidly. Three isomers of tetrachlorocyclohexene react more rapidly than this.* Since the inductive effect of the phenyl group would be expected to increase the rate of bimolecular elimination, the structure of the adduct can hardly accord with these. The two remaining isomers react more slowly than the adduct; the α-isomer has $k_2 = 0{\cdot}007$ l. mole^{-1} sec.$^{-1}$ at 28°; the δ-isomer has $k_2 = 0{\cdot}001$ l. mole^{-1} sec.$^{-1}$. The phenyl derivative of either of these would, it is thought, be more reactive, and the measured value for the adduct is in fact somewhat greater than that of the α-isomer of tetrachlorocyclohexene. So we regard the rate of reaction with alkali as evidence supporting our assignment of the structure of the adduct.

There are several theoretically possible ways in which the adduct could be formed. The routes indicated in the scheme involve *cis*-addition initiated at either the *para*- or

* The unknown structural isomer of tetrachlorocyclohexene and the two extra structural isomers possible for its 1-phenyl derivative would all be expected also to be quite reactive with alkali.

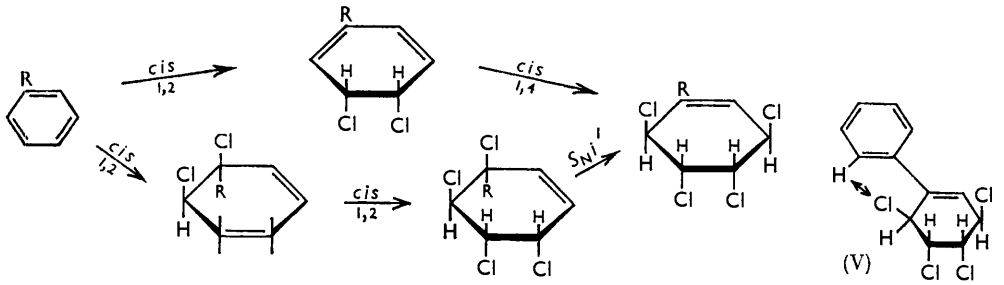
[21] Carlin and Landerl, *J. Amer. Chem. Soc.*, 1953, **75**, 3969; Baddeley, Chadwick, and Taylor, *J.*, 1956, 451.

[22] Orloff and Kolka, *J. Amer. Chem. Soc.*, 1954, **76**, 5484.

[23] Hughes, Ingold, and Pasternak, *J.*, 1953, 3832.

the *ortho*-position; they are mentioned because of the evidence [24] that *cis*-additions of chlorine are sometimes important under similar experimental conditions.

In a conformation (V) in which the phenyl group and the double bond are coplanar, the H–Cl distance (2·26 Å) marked by the arrow implies [25] an overlap of *ca.* 0·7 Å. Relief



of strain by rotation about the Ar–C bond may explain why the extinction coefficient for the adduct ($\varepsilon_{max.}$ 9670) is less than that of phenyl cyclohexene ($\varepsilon_{max.}$ 11,500). A rather more marked effect was noted by Carlin and Landerl [21] for a 6-methyl substituent.

The small reactivity of the adduct with molecular chlorine (in acetic acid at 25°, k_2 = *ca.* 1 × 10^{-4} l. $mole^{-1}$ $sec.^{-1}$) may also partly reflect steric inhibition of conjugation. Such a compound might have been expected, by comparison of reactivities of cinnamyl chloride, allyl chloride, and 1,1-di(chloromethyl)ethylene,[26] to add chlorine at a rate of *ca.* 1 l. $mole^{-1}$ $sec.^{-1}$; so it does not seem that such a low reactivity would be expected for the adduct from polar effects alone. A second, perhaps more important, factor may be that the 3-chlorine atom interferes sterically with the axial attack by the entering chlorine atom; a model shows that attack from the opposite side of the ring will be sterically impeded still more by the axial substituent on the 4- or 5-carbon atom.

It is possible also that the five large substituents attached to the cyclohexene ring in the adduct introduce enough conformational rigidity considerably to reduce the solvolytic reactivity of the 2- and the 5-chlorine substituent; the rate of solvolysis certainly seems rather less than would be expected for a cyclohex-2-enyl chloride,[27] even if allowance is made for the polar effects of the other chlorine atoms.

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