704. *The* ortho : para-*Ratio in Aromatic Substitution. Part III.*[1] *A General Discussion*

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Isomer distributions are reported for the chlorination, by chlorinium ion, of six monosubstituted benzenes. The *ortho* : *para*-ratios are similar to those obtained in nitration. There is no evidence that specific *ortho*-interactions play a part in these reactions, either to facilitate or retard reaction, but the observed trend in *ortho* : *para*-ratios is accounted for in terms of electronic factors. When the reactants are of high reactivity, the *ortho* : *para*-ratio is determined by the relative electron densities at these positions in the ground state, but when they are of low reactivity the ratio is determined by the effect of the substituent on the distribution of charge in the Wheland intermediate, for which there is independent evidence that the amount of charge on the nuclear carbon atoms decreases in the order $p > o > m$.

The factors which govern the relative extents of substitution in the *ortho*- and the *para*-position of a monosubstituted benzenoid compound are not well understood. In some cases there is evidence of steric hindrance to *ortho*-substitution (*e.g.*, in the nitration of t-butylbenzene,[2] and in the acetylation of toluene [3]), and in others there is evidence that interaction between substituent and reagent facilitates *ortho*-substitution (*e.g.*, in the reaction of metal phenoxide ion pairs with formaldehyde,[4] in an alkylation of phenol,[5] and

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[1] Part II, Harvey and Norman, preceding paper.
[2] Nelson and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 5605.
[3] Brown and Young, *J. Org. Chem.*, 1957, **22**, 719.
[4] Peer, *Rec. Trav. chim.*, 1959, **78**, 851; 1960, **79**, 825.
[5] Hart, Spliethoff, and Eleuterio, *J. Amer. Chem. Soc.*, 1954, **76**, 4547.

in the nitration of methyl phenethyl ether[6] and benzyltrimethylsilane[7]). There are other cases in which the *ortho* : *para*-ratio is greater than the statistical value of 2 : 1 but for which the evidence for a facilitating *ortho*-interaction is less strong. For example, it has been proposed that the high *ortho* : *para*-ratio obtained in the nitration of nitrobenzene[8] results from the stabilisation of the transition state for *ortho*-substitution by a dipolar interaction between the substituent and the attacking reagent (NO_2^+).[9] This explanation, however, is not consistent with the high *ortho* : *para*-ratio obtained in the nitration of benzonitrile, for here the corresponding interaction is spatially unsuitable for bonding of the reagent to the *ortho*-position.[10]

So far, most reports of high *ortho* : *para*-ratios (*i.e.*, values greater than 2) have concerned nitration. We have examined the isomer distributions obtained in the chlorination of a number of monosubstituted benzenes with the chlorinium ion, Cl^+. This reagent was chosen because, while it is of similar reactivity to the nitronium ion,[11] it is of different geometry. By comparison of the *ortho* : *para*-ratios obtained in these two reactions, we hoped to determine the importance of specific interactions between substituent and reagent, and whether the electronic theory of aromatic substitution could account for the results observed.

RESULTS AND DISCUSSION

Isomer distributions from the chlorinations studied in the present work, together with those obtained previously (which are italicised), are set out in Table 1, and are compared there with results for nitration of the same compounds.

Isomer distributions for the nitration of nitrobenzene and benzaldehyde were not obtained by modern analytical techniques and are probably not as accurate as the remainder. With this limitation, the *ortho* : *para*-ratios obtained with Cl^+ and with NO_2^+ show marked similarities, the former being rather less selective than the latter. Thus, $\frac{1}{2}o : p$-values decrease gradually in each reaction from nitrobenzene to chlorobenzene (the substituents are arranged in order of increasing nuclear reactivity; see below), and substituents of $-I$, $-M$ character[12] give rise to *ortho* : *para*-ratios greater than 2 with

TABLE 1. *Isomer distributions for the chlorination and nitration of monosubstituted benzenes.*

	Chlorination (Cl^+) (%)				Nitration (NO_2^+) (%)				
Subst.	*o*	*m*	*p*	$\frac{1}{2}o : p$	*o*	*m*	*p*	$\frac{1}{2}o : p$	Ref.
NO_2	17·6	80·9	1·5	5·9	6·4	93·2	0·3	11·0	8
CN	23·2	73·9	2·9	4·0	17·1	80·7	2·0	4·3	*a*
CHO	30·7	63·5	5·8	2·6	(19)	72	(9)	1·0	*b*
CF_3	15·7	80·2	4·1	1·9					
Br	39·7	3·4	56·9	0·35	36·5	1·2	62·4	0·3	*c*
Cl	36·4	1·3	62·3	0·29	29·6	0·9	69·5	0·21	*c*
F					8·7	0	91·3	0·05	11
Me	*74·7*	*2·2*	*23·1*[d]	1·6	58·4	4·4	37·2	0·78	*e*
OMe	*34·9*	*0*	*65·1*[1]	0·27	44·0	2·0[a]	54·0	0·41	*f*

[a] Later work indicates a value of less than 0·1%.[g]

Refs.: *a*, Wibaut and van Strik, *Rec. Trav. chim.*, 1958, **77**, 317. *b*, de la Mare and Ridd, " Aromatic Substitution," Butterworths Scientific Publications, London, 1959, p. 83. *c*, Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525. *d*, de la Mare, Harvey, Hassan, and Varma, *J.*, 1958, 2756. *e*, Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959. *f*, Griffiths, Walkey, and Watson, *J.*, 1934, 631. *g*, Bunton, Minkoff, and Reed, *J.*, 1947, 1416.

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[6] Norman and Radda, *Proc. Chem. Soc.*, 1960, 423.

[7] Chernishev, Dolgaya, and Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 1424.

[8] Holleman, *Chem. Rev.*, 1925, **1**, 187.

[9] Hammond and Hawthorne in " Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley and Sons, Inc., New York, 1956, p. 180.

[10] Hammond and Douglas, *J. Amer. Chem. Soc.*, 1959, **81**, 1184.

[11] Knowles, Norman, and Radda, *J.*, 1960, 4885.

[12] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953.

both reagents. It seems unlikely, therefore, that specific stereochemical interactions govern these *ortho* : *para*-ratios, for in that case differential effects would have been expected to manifest themselves. This conclusion was reached by de la Mare and Ridd,[13] who point out that the similar trends in $\frac{1}{2}o : p$-ratios and $\frac{1}{2}m : p$-ratios in nitration can hardly be coincidental and that the same factors probably determine both ratios. An explanation of the $\frac{1}{2}o : p$-ratios in terms of the electronic factors which are known to govern $\frac{1}{2}m : p$-ratios was therefore sought.

Strong evidence has accumulated that the principle enunciated by Hammond with reference to the structure of the transition state [14] is applicable to aromatic substitution: [11] namely, that the transition state resembles the reactants when these are of high reactivity, and the Wheland intermediate when they are of low reactivity. The implications of each of these assumptions will be examined separately.

Reactants of Low Reactivity.—As an approximation, the transition state may be taken to have the same structure as the Wheland intermediate, *i.e.*, to be a resonance hybrid of the canonical structures (I), (II), and (III). The simplest picture of the distribution of charge in the hybrid ion is one in which this charge is equally shared between three carbon atoms (IV), as predicted by the simple Hückel treatment.[15] Recently, evidence has been adduced that these carbon atoms do not share the charge equally. From nuclear magnetic resonance measurements of the proton shifts in the pentamethylcyclohexadienyl cation (V) it has been found that the positive charge in the cyclohexadienyl cation is rather more heavily concentrated in the *para*- than in the *ortho*-position, the distribution being indicated in (VI).[15] The calculated positive charge densities for this ion, obtained by a perturbation method allowing for electron interaction,[15] and shown in (VII), show the same order of charge densities ($p > o > m$) as the nuclear magnetic resonance experiments, although the absolute values differ slightly. Similarly, nuclear magnetic resonance measurements of the chemical shifts of the ring protons show the same order of positive-charge densities in the Ph_3C^+ ion.[16]

The higher concentration of charge in the *para*- than in the *ortho*-position is equivalent to a greater importance of structure (III) as a contributor to the hybrid (IV) than of (I) and (II). This can be understood by the principles of electron correlation,[17] in that the four π-electrons in the residual aromatic system in the σ-complex (IV) tend to be distributed in pairs, the pairs lying as far from each other as possible, *i.e.*, on opposite sides of the nucleus. That is, (III) is the most probable electronic configuration. This is a rationalisation of the view that conjugative interaction is more effective at the *para*- than at the *ortho*-position.[18]

It follows that any substituent group will exert a more powerful effect on the stability of the hybrid ion (IV) when it is *para* to the entering reagent than when it is *ortho*, and a more powerful effect when it is *ortho* than when it is *meta*. For example, the electron-attracting NO_2 group will destabilise the ion (IV) increasingly in the order $m < o < p$, while the electron-releasing methyl group will stabilise it increasingly in the same order. Thus, when the transition state resembles the intermediate, electron-attracting substituents will give rise to the orientation $m > o > p$, and electron-releasing substituents to the reverse order. By the Hammond postulate, this should be valid for the reactions of unreactive aromatic compounds such as nitrobenzene with fairly reactive reagents such as the Cl^+ and NO_2^+ ions, and of fairly reactive aromatic compounds with very unreactive reagents such as molecular chlorine. These predictions are consistent with experiment (see Tables 1 and 2).

For benzenoid compounds where the substituent is of $-I$, $-M$ type, not only are the

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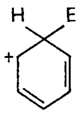
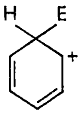
[13] Ref. *b* of Table 1, p. 82.
[14] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.
[15] Mackor, paper given at the Ampère conference in Pisa, 1960 (personally communicated).
[16] O'Reilly and Leftin, *J. Phys. Chem.*, 1960, **64**, 1555.
[17] Dickens and Linnett, *Quart. Rev.*, 1957, **11**, 291.
[18] Waters, *J.*, 1948, 727; de la Mare, *J.*, 1949, 2871.

high *ortho* : *para*-ratios rationalised by the above argument, but so is the variation in $\frac{1}{2}o : p$-ratios apparent from Table 1 for chlorination and nitration ($Ph{\cdot}NO_2 > Ph{\cdot}CN > Ph{\cdot}CHO > Ph{\cdot}CF_3$). The nuclear reactivity of these molecules, though not quantitatively studied, should lie in the order[11] $Ph{\cdot}NO_2 < Ph{\cdot}CN < Ph{\cdot}CHO \sim Ph{\cdot}CF_3$, since the electron-attracting capacities of the substituents (measured by their σ-values *) decrease in this order.[19] As the reactivity of the molecule decreases, the transition state



(I)



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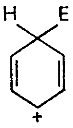

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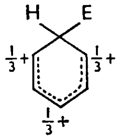

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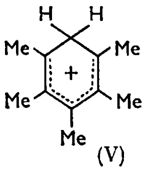
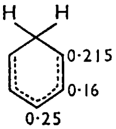
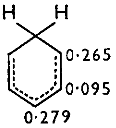


(V)



(VI)



(VII)

should resemble the Wheland intermediate more closely, so that the proportion of the ultimate positive charge which the aromatic system accommodates in the transition state should increase in the order $Ph{\cdot}CF_3 \sim Ph{\cdot}CHO < Ph{\cdot}CN < Ph{\cdot}NO_2$. Hence the differential effect which operates to retard *para*- more than *ortho*-substitution should increase in this order and the $\frac{1}{2}o : p$-ratio should be greatest for $Ph{\cdot}NO_2$ and least for $Ph{\cdot}CF_3$ and Ph·CHO.

Reactants of High Reactivity.—The transition state in these reactions should involve only minor deformation of the aromatic system, so that the relative reactivities of *ortho*- and *para*-positions should be determined by the relative electron densities at these positions in the ground state.[11] σ-Values (or, more strictly, σ_G-values[20]), which are a measure of these electron densities, are not known for *ortho*-positions, but (restricting discussion for the present to toluene) there is evidence that the *ortho*-position is more negatively polarised than the *para*-position. First, the inductive effect of a substituent operates more powerfully on the *meta*- than on the *para*-position, as shown, for example, by the σ-values of the *m*- and p-NMe_3^+ groups (0·88 and 0·82 respectively[19]), and it is a reasonable extension of this result that it operates more powerfully on the *ortho*- than on the *para*-position. Secondly, there is evidence that the resonance polar effect of a substituent conjugated to the aromatic nucleus is small when conjugation is " sacrificial: "[21] the resonance polar effect is only about 10% of the total polar effect of the p-NO_2 group.[22] The same should be true of the *p*-Me group, for which, in any case, there is little evidence that mesomeric release is significant in the ground state.[23] It is therefore reasonable to conclude that the methyl group induces a higher electron density at the *ortho*- than at the *para*-position, so that the *ortho*-position should be more reactive towards reagents of high reactivity when, by the Hammond postulate, the transition state involves little deformation of the aromatic system. This is true of the reactions of toluene with the very reactive reagents (primarily 'onium ions) involved in chlorination by chlorinium bion,romination by brominium ion, detritiation, and bromodesilylation (see Table 2).† On the other hand, with less reactive reagents such as molecular chlorine and bromine, and deuterium bromide, toluene gives rise to $\frac{1}{2}o : p$-ratios less than unity.

The reactions of toluene are conveniently represented graphically. Reactions of

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* The σ-value of *p*-CHO is not known accurately. It should be somewhat larger than that of *p*-COMe (0·50) and therefore about the same as that of p-CF_3 (0·54).

† The large proportion (80%) of *o*-nitro-derivative obtained by nitration of $Ph{\cdot}CH_2{\cdot}SiMe_3$ was interpreted by Eaborn and Parker[25] in this way, since the $-CH_2{\cdot}SiMe_3$ group is strongly electron-releasing ($\sigma_p = -0{\cdot}26$).

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

[20] Norman, Radda, Brimacombe, Ralph, and Smith, *J.*, 1961, in the press.

[21] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.

[22] Wepster, *Rec. Trav. chim.*, 1956, **75**, 1473.

[23] Conference on " Hyperconjugation," *Tetrahedron*, 1959, **5**, 105—274; Ferreira, *Nature*, 1950, **188**, 848.

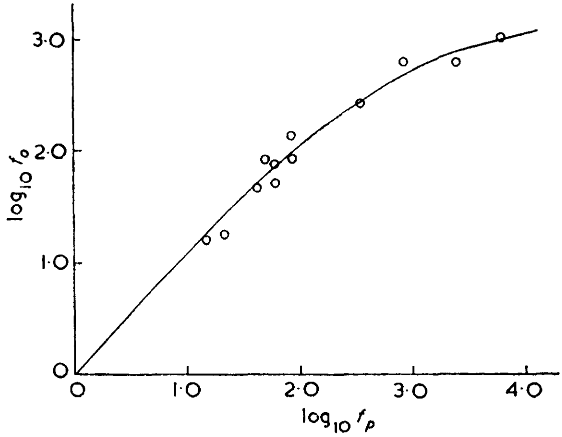
toluene were chosen for the plot in the Figure for which steric hindrance to *ortho*-substitution seemed likely to be small. Thus, data for Friedel–Crafts reactions and for mercuration were omitted since there is evidence that these reactions are subject to steric hindrance.[3, 24] The reactions selected, and the data appropriate to them, are set out in Table 2.

TABLE 2. *Partial rate factors for* ortho- *and* para-*substitution in toluene.*

Reaction	$\log_{10} f_o$	$\log_{10} f_p$	Reaction	$\log_{10} f_o$	$\log_{10} f_p$
Protodesilylation ($Ph{\cdot}SO_2{\cdot}OH$) [a]	1·20	1·16	Chlorination (Cl^+) [f]	2·13	1·91
Protodesilylation ($HClO_4$) [b]	1·25	1·32	Deuteration (68% H_2SO_4) [g]	1·92	1·92
Detritiation [c]	1·67	1·61	Deuteration ($CF_3{\cdot}CO_2H$) [h]	2·42	2·54
Bromodesilylation [d]	1·91	1·69	Chlorination (Cl_2) [i]	2·79	2·91
Bromination (Br^+) [e]	1·88	1·77	Bromination (Br_2) [j]	2·78	3·38
Nitration [11]	1·70	1·78	Deuteration (DBr) [k]	3·00	3·78

Refs.: *a*, Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323. *b*, Eaborn, *J.*, 1956, 4858. *c*, Melander, *Acta Chem. Scand.*, 1956, **10**, 879. *d*, Deans, Eaborn, and Webster, *J.*, 1959, 3031. *e*, de la Mare and Harvey, *J.*, 1956, 36. *f*, Ref. *d* of Table 1. *g*, Gold and Satchell, *J.*, 1956, 2743. *h*, Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309. *i*, Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175. *j*, Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421. *k*, Shatenstein, Kalinachenko, and Varshavskij, *Zhur. fiz. Khim.*, 1956, **30**, 2098.

The graph illustrates the trend for values of $\tfrac{1}{2}o : p$-ratios greater than unity when $\log_{10} f_p$ is rather small (corresponding to reagents of low selectivity and high reactivity [26]) and values less than unity when $\log_{10} f_p$ is large (corresponding to high selectivity and low reactivity [26]). The curve passes through the origin since a reagent of infinite reactivity would be unselective, *i.e.*, $\log_{10} f_o$ would equal $\log_{10} f_p$, and both would be equal to zero.



Plot of $\log_{10} f_o$ *against* $\log_{10} f_p$ *for reactions of toluene.*

Substituents of —I, +E *Type*.—Halogen and methoxyl substituents withdraw electrons from the aromatic ring by the —*I* mechanism, but release electrons mesomerically. The —*I* effect should operate most powerfully on the *ortho*-position, so that this is more deactivated to electrophiles than the *para*-position when the reagent is of high reactivity. When the reagent is of lower reactivity, so that the distribution of electrons in the Wheland intermediate is of importance in determining the relative reactivities, the full potential of the substituent to stabilise the ion by its mesomeric effect is brought into operation.[11] Since positive charge is most highly concentrated in the *para*-position in the intermediate, a substituent of +*E* character exerts its strongest influence when the reagent adds to this position. Thus, when the transition state resembles either reactants or intermediate, the $\tfrac{1}{2}o : p$-ratio should be less than unity, and this is consistent with experiment (Tables 1

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[24] Brown and McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2300.

[25] Eaborn and Parker, *J.*, 1954, 939.

[26] Nelson, *J. Org. Chem.*, 1956, **21**, 145; Brown and Smoot, *J. Amer. Chem. Soc.*, 1956, **78**, 6255.

and 3). The $-I$ effect of the halogens and their $+E$ effects both decrease in the order F > Cl > Br. Hence, in all reactions, both the differential effects outlined above should operate most powerfully in fluorobenzene and least in bromobenzene. This is borne out experimentally, whereas if the observed $\frac{1}{2}o:p$-ratios resulted from steric hindrance to *ortho*-substitution, they should be least for bromobenzene.

TABLE 3. *The reactions of anisole and the halogenobenzenes* : $\frac{1}{2}$o : p-*ratios.*

Reaction	Ph–OMe	Ph–F	Ph–Cl	Ph–Br
Chlorination (Cl_2) [8, 27]	0·13		0·35 *	0·40 *
Bromination (Br_2) [28]	~0·02	0·06 *	0·06 *	0·08 *

* Catalysed by metal halides.

In summary, *ortho* : *para*-ratios in reactions in which specific *ortho*-effects are not significant, are satisfactorily accounted for by application of the Hammond postulate. When, with reactants of high reactivity, this predicts that the transition state involves little deformation of the aromatic system, the ratio is determined by the relative electron densities at the *ortho*- and *para*-positions in the ground state; whereas when the reactants are of lower reactivity, it is determined by the relative stabilities of the appropriate Wheland intermediates. These may be predicted by application of the principles of electron correlation.

EXPERIMENTAL

Materials.—Benzaldehyde, benzonitrile, benzotrifluoride, bromobenzene, chlorobenzene, and nitrobenzene and their monochloro-derivatives were commercial materials, except *o*-bromochlorobenzene, *o*-dichlorobenzene, and *m*-chlorobenzonitrile which were prepared from the corresponding chloroanilines by the Sandmeyer reaction. All materials were purified by fractional distillation or recrystallisation to constant m. p. from light petroleum of various boiling ranges. Benzaldehyde and *o*-chlorobenzaldehyde were washed with 10% sodium carbonate solution before distillation and were distilled in the presence of a small amount of catechol. *m*-Chlorobenzaldehyde was purified by low-temperature recrystallisation from light petroleum (b. p. 40—60°).

Chlorinations.—Chlorinations were carried out at 25°. To a saturated solution of chlorine (0·7 g., <0·1 mole) in carbon tetrachloride (B.D.H. "AnalaR") was added the aromatic compound (0·1 mole), 62% perchloric acid (10 ml.), and silver perchlorate (0·05 mole).[29] The mixture was shaken for a time varying from 30 min. to 8 hr. (depending on the reactivity of the compound chlorinated), then water was added to the solution, and the whole was extracted four times with carbon tetrachloride. The extracts were shaken with sodium hydrogen sulphite (except in the chlorination of benzaldehyde where unchanged chlorine was removed by bubbling nitrogen through the solution), and the solvent was removed.

Dichlorination could not be detected under these conditions, although some occurred in the chlorination of chlorobenzene and bromobenzene if the reaction was allowed to proceed for more than 30 min. It was also found that the time needed to obtain a sufficient degree of chlorination of nitrobenzene, benzonitrile, and benzotrifluoride for analysis of the chloro-products was much shorter if a two- or three-fold excess of chlorinating agent was used. Under these conditions there was no evidence of dichlorination.

Analysis.—The reaction mixtures were analysed by gas chromatography and infrared spectroscopy.

Gas-chromatographic analysis. The details of the column conditions and retention times of the individual isomers are shown in Table 4. The results, each of which is the mean of at least three analyses, are shown, together with the mean deviations, in Table 5. Where the proportion of *meta*- and *para*-isomers is not shown separately these isomers were not resolved on the column.

Spectroscopic analysis. The monochloro-isomers were separated from the unchanged starting material by gas chromatography and were collected in a cold trap at −70°, followed by an

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[27] Jones and Richardson, *J.*, 1956, 3939.

[28] de la Mare and Vernon, *J.*, 1951, 1764; Ferguson, Garner, and Mack, *J. Amer. Chem. Soc.*, 1954, **76**, 1250.

[29] Ref. *b* (p. 107) of Table 1.

TABLE 4. *Gas-chromatographic results.*

Compound	Column	Temp.	Flow (ml./min.) of N_2	Retention time (min.)
o-Chloronitrobenzene	2,4,7-Trinitrofluorenone (10%).† Length: 400 cm.*	178°	62	43
m-Chloronitrobenzene				34
p-Chloronitrobenzene				38
o-Chlorobenzonitrile	Tritolyl phosphate (20%). Length: 203 cm.	150	50	55
m-Chlorobenzonitrile				40
p-Chlorobenzonitrile				36
o-Bromochlorobenzene	Tritolyl phosphate (20%). Length: 203 cm.	115	55	55
m-Bromochlorobenzene				44
p-Bromochlorobenzene				44
o-Dichlorobenzene	Tritolyl phosphate (20%). Length: 203 cm.	100	55	48
m-Dichlorobenzene				37
p-Dichlorobenzene				37
o-Chlorobenzotrifluoride	Polyethylene glycol (5%) and stearic acid (2%). Length: 200 cm.	60	70	40
m-Chlorobenzotrifluoride				18
p-Chlorobenzotrifluoride				22

* On firebrick. The other columns had Embacel as inert support.
† Norman, *Proc. Chem. Soc.*, 1958, 151.

TABLE 5. *Gas-chromatographic analysis.*

	Isomer distribution		
Compound	*o*-Chloro (%)	*m*-Chloro (%)	*p*-Chloro (%)
Benzonitrile	22·6 ± 1·4	77·4 ± 1·5	
Bromobenzene	38·5 ± 1·0	61·5 ± 1·0	
Chlorobenzene	36·1 ± 0·5	63·9 ± 0·5	
Nitrobenzene	17·6 ± 0·3	80·9 ± 0·5	1·5 ± 0·4
Benzotrifluoride	15·7 ± 0·5	80·2 ± 0·5	4·1 ± 0·4

electrostatic precipitator at 15,000 v. The column (200 cm. × 4·5 mm.) was packed with Apiezon "L" grease (20% w/w) coated on Embacel and was operated at temperatures between 130° and 150° with nitrogen (62 ml./min.) as carrier gas. Synthetic mixtures were analysed before and after collection by infrared spectroscopy. Results confirmed that the collection technique was quantitative.

The spectroscopic analyses were carried out with a Perkin–Elmer Recording infrared spectrophotometer (model 21). Investigations in the 10—15 μ region for solutions of the pure chloro-isomers in carbon disulphide ("AnalaR") showed that in each of the groups of the three monochloro-isomers each isomer had a characteristic absorption band (see Table 6). The molecular extinction coefficients were measured from the optical densities of standard solutions. The isomer ratios obtained (Table 6) are averages of at least three analyses. The agreement between the isomer ratios obtained by the two methods of analysis is within 2%.

TABLE 6. *Infrared analysis.*

	Isomer distribution			Wave-length		
Compound	*o*-Chloro (%)	*m*-Chloro (%)	*p*-Chloro (%)	*o*- (μ)	*m*- (μ)	*p*- (μ)
Benzaldehyde	30·7 ± 0·6	63·5 ± 1·1	5·8 ± 0·3	9·7	11·5	9·9
Benzonitrile	23·9 ± 1·0	73·2 ± 1·0	2·9 ± 0·1	13·2	12·7	12·1
Bromobenzene	40·9 ± 0·6	3·4 ± 0·9	55·7 ± 1·5	13·4	12·9	12·3
Chlorobenzene	36·7 ± 0·4	1·3 ± 0·5	62·0 ± 0·5	13·4	12·8	12·2

Some oxidation occurred during the chlorination of benzaldehyde. A mixture of chlorobenzoic acids (0·2 g.) was isolated from the main product, which contained chlorobenzaldehydes (3·1 g.). Infrared spectroscopic analysis of the chlorobenzoic acids gave the following approximate ratios: *ortho*- 20%, *meta*- 80%, *para*- <1%. From these figures, the maximum error in the isomer distribution in the chlorination of benzaldehyde is within the accuracy of the method of analysis even if all the chlorobenzoic acids were formed by oxidation of chlorobenzaldehydes.

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