Vapour Phase Chemistry of Arenes. Part II.[1] Thermolysis of Chlorobenzene and Reactions with Aryl Radicals and Chlorine and Hydrogen Atoms at 500°

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Pyrolysis of chlorobenzene is interpreted as a radical (chain) process with the radicals $\cdot C_6H_4Cl$, $\cdot Cl$, and $H\cdot$ as carriers. Chlorobenzene, with added sources of $R\cdot$ ($Cl\cdot$, $H\cdot$, or $Ph\cdot$) gives the biaryls chlorobiphenyl and bichlorophenyl, the ratio being highly dependent on $R\cdot$. Thus, $Cl\cdot$ mainly abstracts H from PhCl to give *o*, *m*, and *p*-$\cdot C_6H_4Cl$ radicals (20:55:25) forming bichlorophenyls as the main product, whereas $H\cdot$ replaces and abstracts chlorine; $Ph\cdot$ leads to chlorobiphenyls as the principal products. Isomer distributions have been determined and are discussed. It is also shown that $\cdot C_6H_4Cl$ radicals are isomerically stable under our conditions (*e.g.*, *m*-$\cdot C_6H_4Cl$ + PhH $\longrightarrow$ 3-ClC_6H_4Ph only). With *o*-$\cdot C_6H_4Cl$, naphthalene is formed in addition to 2-chlorobiphenyl. However, benzyne is rejected as an intermediate. *ortho*-Dichlorobenzene and biphenyl are found to react with $H\cdot$ at comparable rates.

THE thermolysis of chlorobenzene at 700—800° has been previously investigated.[2,3] Apart from H_2 and HCl,[2] organic products were bichlorophenyls and chlorobiphenyls (*ca.* 4 : 1). On mass spectral evidence,[3] traces of naphthalene, chloronaphthalene, and biphenylene were also formed (<1%). Cullis and Manton[2] postulated a radical chain reaction with $Cl\cdot$ and $\cdot C_6H_4Cl$ as principal carriers. Fields and Meyerson[3] considered (molecular) loss of HCl to give benzyne a likely competitive pathway; benzyne would

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[1] Part I, R. Louw and H. J. Lucas, *Rec. Trav. chim.*, 1973, **92**, 55.

[2] C. F. Cullis and K. Priday, *Proc. Roy. Soc.*, 1954, *A*, **224**, 308; C. F. Cullis and J. E. Manton, *Trans. Faraday Soc.*, 1958, **54**, 381.

[3] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, 1966, **88**, 3388.

lead to chlorobiphenyl by insertion and to (chloro)-naphthalene *via* addition to chlorobenzene.

Recently[1] we have considered the mechanism of the thermolysis of benzene and biphenyl; it was concluded that a chain process involving hydrogen atoms and aryl radicals obtained. In the course of our study on the vapour phase chemistry of benzene derivatives[1,4,5] we have also investigated the thermolysis of chlorobenzene. The amount and the composition of the biaryls (biphenyl, chlorobiphenyls, bichlorophenyls) produced upon thermolysis at 500° under nitrogen are compared with those from reactions involving added chlorine, formaldehyde, azobenzene, and allyl benzoate as sources of Cl•, H•, and Ph•, respectively.

We report that on experimental and thermochemical grounds the thermolysis of chlorobenzene is a radical chain reaction involving $\cdot C_6H_4Cl$, H•, and Cl• as carriers. Moreover we have checked that (independently generated) *meta*- or *para*-$\cdot C_6H_4Cl$ radicals do not isomerise under our conditions. *ortho*-$\cdot C_6H_4Cl$ rather than benzyne is proposed as the precursor for the by-product naphthalene.

RESULTS AND DISCUSSION

Effect of Additives.—We employed our usual flow reactor system, operating at atmospheric pressure with nitrogen as the carrier gas.[6] The data on representative runs (Table 1) show that both the amount and the composition of the biaryls formed are markedly influenced by additives. These facts (which agree with those reported for benzene as a substrate) strongly point to free radical mechanisms throughout.

TABLE 1

Biaryls from chlorobenzene at 500 ± 10°; effect of additives

No.	Conditions PhCl [a]	Additive [a]	Average residence time(s)	Ph$_2$	Proportion of biaryls formed PhC_6H_4Cl (A)	$ClC_6H_4C_6H_4Cl$ (B)	A : B
1 [b]	310	Cl_2, 3—7	120	(0·3)	7	91	0·08
2 [c]	80	None	110	(<5)	15	85	0·23
3 [d]	114	H_2CO, 12	114	4	44	51	0·9
4 [e]	285	PhN=NPh, 5	105	9	52	39	1·3
5 [g]	89	AB,[f] 17	120	15	85	(<5)	>10
6 [h]	88	{AB,[f] 19 {H_2CO, 9	118	15	85	(<5)	>10

[a] Flow rates, in mmol h^{-1}; nitrogen (carrier gas) was in a 2—4 fold excess over chlorobenzene. [b] At 400°; complete chlorine conversion; 60—80% yield of $PhCl_2$ ($o : m : p = 15 : 61 : 24$); 10—30% of (di)chlorobiphenyls; product also contains small amounts (<1%) of trichlorobiphenyl, trichloroterphenyl, and dichloroterphenyl, as shown by mass spectrometry. Without chlorine there is no product observed (*cf.* note *d*). [c] The decomposition level of chlorobenzene is *ca.* 0·05—0·1%; our A : B ratio tallies well with that reported by Fields and Meyerson (690°).[3] [d] Biaryls *ca.* 1% based on original PhCl; HCl is formed, as is benzene (*ca.* 1%); $PhCl_2$ is only 4% based on benzene. H_2CO Was introduced as a solution of trioxan in benzene readily giving 3 mol. equiv. of formaldehyde,[7] 10—30% of the latter decomposing, judging from CO production[8] (g.l.c.). [e] Azobenzene conversion 30%; biaryl 1·0% based on original PhCl (or 1·4 mol per mol of azobenzene converted); benzene 1·6 mol per mol of azobenzene. [f] Allyl benzoate; conversion 30—40%.[9,10] [g] PhC_6H_4Cl 1·8%, HCl 0·4% (both based on original PhCl). [h] PhC_6H_4Cl 1·8%, HCl 0·3% (based on PhCl).

Mechanistic Considerations.—The pyrolysis of chlorobenzene can be initiated by reaction (1) or by other radical forming steps;[1] these may involve additives (or, in their absence, impurities). As relevant chain-propagating steps we consider reactions (2)—(9) which are given with activation parameters outlined in the Appendix.

The product ratio (Ph_2) : (PhC_6H_4Cl) : ($ClC_6H_4C_6H_4Cl$) will reflect the ratio of Ph• and $ClC_6H_4\cdot$ radicals formed as intermediates. This ratio is governed by the additives; it depends on the properties and the concentrations of the 'added' radicals Ph• (from azobenzene or allyl acetate), H• (from formaldehyde), or Cl• (from chlorine). Thus, the reaction with a little Cl_2 (experiment 1), proceeding *via* reaction (2), constitutes a homolytic chlorophenylation of PhCl [step (8)], a process accompanied by replacement of a chlorine substituent [reaction (9)]. Our data indicate k_9/k_8 *ca.* 0·08.* Judging from the very small amount of biphenyl formed [reaction (4)], Ph• is only formed to a minor degree, route (8)–(5)–(4) being apparently inefficient. In fact, not only $\cdot C_6H_4Cl$ but also H• and Ph• will react mainly with chlorine [reaction (10)] (see note *b*, Table 1), the sequence leading to biaryls thus chiefly consisting of reactions (2), (8) + (9), and (10).

In mere thermolysis (experiment 2), however, the (H•) : (Cl•) and the (Ph•) : ($ClC_6H_4\cdot$) ratios are expected to be larger; reactions (5) and (3) + (4) now contribute to a substantial degree. Apart from $\cdot C_6H_4Cl$ and •Cl, suggested by Cullis and Manton,[2] we therefore also consider H• as a principal carrier in chlorobenzene pyrolysis.

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* For comparison, a 1 : 1 mixture of benzene and *ortho*-dichlorobenzene with 3 mole % of azobenzene at *ca.* 500° (see experiment 4) leads to the following biaryls (relative amounts, given as peak area ratios from g.l.c. analysis): Ph_2 (1), *o*-Ph•-C_6H_4Cl (0·20), 2,3-$Cl_2C_6H_4Ph$ (0·15), 3,4-$Cl_2C_6H_4Ph$ (0·53). After statistical correction the ratio analogous to k_9/k_8 is thus found to be $\frac{1/2(0{\cdot}20)}{5/4(0{\cdot}68)}$ or *ca.* 0·12.

[4] J. W. Rothuizen, Thesis, Leiden, 1967; W. Dorrepaal and R. Louw, *Rec. Trav. chim.*, 1971, **90**, 700, and earlier papers in this series.

[5] W. Dorrepaal, Thesis, Leiden, 1972.

[6] R. Louw and E. C. Kooyman, *Rec. Trav. chim.*, 1965, **84**, 1511.

[7] W. Hogg, D. M. McKinnon, A. F. Trotman-Dickinson, and G. J. O. Verbeke, *J. Chem. Soc.*, 1961, 1403.

[8] C. J. Chen and D. J. McKenney, *Canad. J. Chem.*, 1972, **50**, 992.

[9] R. Louw and J. W. Rothuizen, *Tetrahedron Letters*, 1967, 3807.

[10] R. Louw and E. C. Kooyman, *Rec. Trav. chim.*, 1967, **86**, 147.

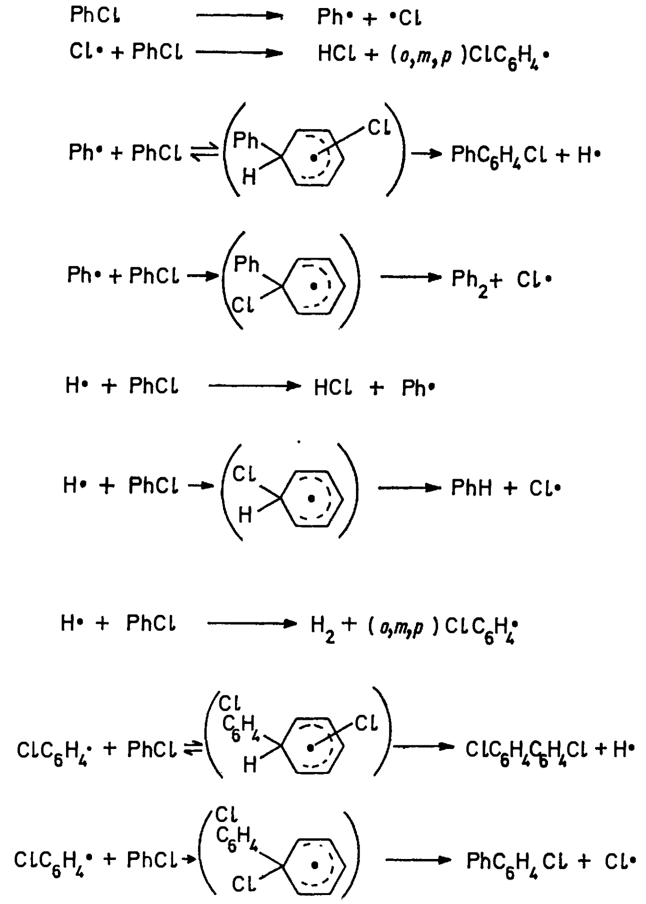
This trend is seen when formaldehyde (experiment **3**) is involved; this introduces (additional) atomic hydrogen, *via* reactions (11) and (12),[8] increasing the (H•) : (Ar•) ratio. The product pattern observed can be considered as the sum of both phenylation [steps (3) and (4)] and chlorophenylation [steps (8) and (9)] in a ratio of

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \quad (R = \text{aryl or hydrogen}) \quad (10)$$

$$H_2CO \longrightarrow H\cdot + (\cdot CHO) \longrightarrow H\cdot + CO \quad (11)$$

$$R\cdot(\text{aryl or } Cl\cdot) + H_2CO \longrightarrow RH + (\cdot CHO) \longrightarrow H\cdot + CO \quad (12)$$

ca. 0·5; accepting $k_4/k_3 = k_9/k_8 = 0{\cdot}1$ and $k_3 = k_8$ this also means (Ph•) : (•C_6H_4Cl) *ca.* 0·5. Addition of azobenzene (run 4) is then found to lead to (Ph•) : (•C_6H_4Cl) *ca.* 1. The azobenzene acts as a source of phenyl radicals effecting homolytic phenylation of chlorobenzene;[9] in addition, chlorobenzene 'pyrolysis' (mainly giving $ClC_6H_4C_6H_4Cl$) is enhanced *via* reactions (3) and (4). With allyl benzoate as source of phenyl radicals[9] (run 5) this induced thermolysis is suppressed by the allyl groups. Thus, phenylation [reaction (3)] is now the main process. Addition of some formaldehyde to this system (run 6) has hardly any or no additional effect.



(1); $\log k_1 = 15 - 93/2{\cdot}303RT$ *

(2); $\log k_2 = 12 - 8/2{\cdot}303RT$

(3); $\log k_{3\,\text{eff}} = 11 - 4/2{\cdot}303RT$

(4); $\log k_4 = 12 - 10/2{\cdot}303RT$

(5); $\Delta H_5 = -10$

(6); $\log k_6 = 13 - 4/2{\cdot}303RT$

(7); $\log k_7 = 13 - 12/2{\cdot}303RT$

(8); $\log k_{8\,\text{eff}} \sim \log k_{3\,\text{eff}}$

(9); $\log k_9 \sim \log k_4$

* Units: ΔH and RT in kcal mol^{-1}; t in s, concentration in mol ml^{-1}.

Isomer Distributions.—We have also determined the isomer compositions of PhC_6H_4Cl and $ClC_6H_4C_6H_4Cl$. According to the data in Table 2 the PhC_6H_4Cl distributions, although somewhat varying, are of the same type. We have proposed two modes of formation, *viz.* reaction (9), thought to predominate in run 1, and reaction (3), the process involved in runs 5 and 6. The observation of an essentially unchanged isomer pattern suggests that the isomeric •C_6H_4Cl radicals are formed in a highly comparable distribution. This is consonant with the isomer distributions formed for $ClC_6H_4C_6H_4Cl$; the pattern shown in Table 2 is seen to be similar to that calculated for arylation of chlorobenzene by •C_6H_4Cl ($o:m:p = 21:52:27$) if each isomeric radical is supposed to give the same (21 : 52 : 27) arylation pattern and will have the same k_8 (see Table 2, last line *).

This 'characteristic' isomer distribution raises the

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* This pattern is also comparable, but not identical, with that observed for chlorination of chlorobenzene in the vapour phase under comparable conditions[4,5] ($PhCl \longrightarrow C_6H_4Cl_2$, $o:m:p \longrightarrow 15:60:25$). We believe that this is caused by slight differences in relative rates of reactions (8) and (10) for *o*-, *m*-, and *p*-ClC_6H_4•, respectively.

question whether thermodynamic factors play an important (or even decisive) role. One might consider the possibility that $\cdot C_6H_4Cl$ radicals isomerise rapidly, leading to an equilibrium composition. We have performed control experiments which show that, *e.g.* p-$\cdot C_6H_4Cl$ radicals, once formed, retain their identity under the present experimental conditions. Thus, thermolysis of chlorobenzene at 500° with added *p,p'*-dichloroazobenzene leads to biaryls with the composition described for run 4 (Table 1), with, however, additional quantities of *o,p'*-, *m,p'*-, and *p,p'*-$ClC_6H_4C_6H_4Cl$, in a ratio of 21 : 52 : 27. This additionally formed p-$ClC_6H_4C_6H_4Cl$ amounted to 42% relative to the $ClC_6H_4C_6H_4Cl$ produced from chlorobenzene *per se*. Likewise, thermolysis of benzene with added allyl esters of *p*- or *m*-chlorobenzoic acid gives the corresponding PhC_6H_4Cl to the exclusion of other isomers. The same holds for reactions involving $\cdot C_6H_4Cl$ radical from allyl *o*-chlorobenzoate; here, however, naphthalene is also produced.

TABLE 2

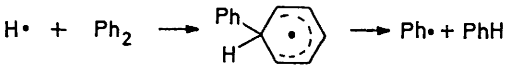
Isomer distributions of chlorobiphenyls

No. (see Table 1)	PhC_6H_4Cl			$ClC_6H_4C_6H_4Cl$					
	o	*m*	*p*	*o,o'* [a]	*o,m'*	*o,p'*	*m,m'*	*m,p'*	*p,p'*
1	21	52	27 [a]	5	22	12	26	28	7
2				5	21	11	29	27	7
3	20	56	24 [a]	5	23	11	29	27	5
4	22	53	25 [a]				*b*		
5	25	48	27						
6	26	46	27						
c	(21)	(52)	(27)	4·4	21·8	11·4	27·0	26·0	7·3

[a] *p*-PhC_6H_4Cl and *o,o'*-$ClC_6H_4C_6H_4Cl$ were not separated by g.l.c. under our conditions. We have arbitrarily divided the surface area so as to obtain maximum consistency. [b] Not analysed quantitatively; the pattern was seen to be analogous, if not identical to that of runs 1—3. [c] Calculated for arylation by $\cdot C_6H_4Cl$ (with $o : m : p = 21 : 52 : 27$), all three isomeric radicals leading to the same isomer pattern with identical rates (see text).

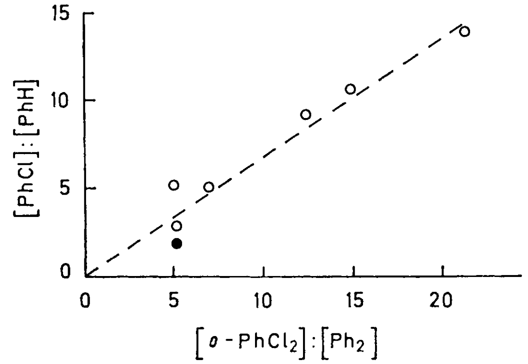
Hydrogenolysis.—Replacement of substitients in benzene derivatives PhZ by atomic hydrogen to give benzene is well known for Z = Me.[11] In comparable fashion, chlorobenzene may give HCl *via* reactions (6) and/or (5). In a 'blank' pyrolysis of PhCl at 500° and residence times about 2 min, the amounts of HCl and benzene formed were <0·1%. In the presence of formaldehyde, the rates of formation, as were those for biaryls, were increased. Typically, chlorobenzene (160 mmol h^{-1}) + formaldehyde (30) led to CO (10—20), HCl, and benzene (0·6—0·8 each). Comparable results were obtained with *ortho*-dichlorobenzene, giving HCl and chlorobenzene; benzene is not observed as a product.

We have stated[1,9] that addition of Ph· to arene is reversible at 500°; consequently, biphenyl may also react with H· to give benzene and Ph· under these conditions [reaction (13)]. We have studied the thermolysis of mixtures of *ortho*-dichlorobenzene and Ph_2 with added formaldehyde as a source of H· atoms. Indeed, both chlorobenzene and benzene are produced. The ratio of these hydrogenolysis products (chlorobenzene : benzene) as a function of the intake ratio *o*-dichlorobenzene : biphenyl is seen in the Figure.



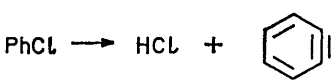
(13)

The apparent relative rate is close to unity; this tallies well with the fact that H· atom reactions with substituted benzenes are almost insensitive to substituent effects.[12] There are, however, some complicating factors. First, reaction (13) will give between 1 and 2 equiv. of benzene per H· atom involved. Moreover, we are presently unable to estimate k_5/k_7 (although both processes are expected to give one HCl per H· atom). Therefore, the result cannot yet be identified with individual steps. It does demonstrate, in our opinion, the operation of free hydrogen atoms.



Formation of hydrogenolysis products from *ortho*-dichlorobenzene–biphenyl mixtures at *ca.* 500°: ○ with added formaldehyde; ● without additive

Benzyne as Possible Intermediate.—As mentioned briefly in the introduction, Fields and Meyerson,[3] when pyrolysing chlorobenzene at 690°, found small amounts of naphthalene (0·3% of $ClC_6H_4C_6H_4Cl$) and chloronaphthalene (0·1%), together with biphenylene (0·5%). These by-products were thought to arise through benzyne, formed *via* step (14), benzyne then leading to (chloro)naphthalene [and (chloro)acetylene] *via* 1,4-addition to chlorobenzene.[13] These workers also studied the product composition ftom the pyrolysis of 2 mole % of phthalic anhydride (which is known to give benzyne by loss of CO_2 and CO) in PhCl at 690°. Here, chloronaphthalene is an important product (*ca.* 30% of $ClC_6H_4C_6H_4Cl$); however, naphthalene is still only 3% of $ClC_6H_4C_6H_4Cl$. In our opinion, therefore,



(14)

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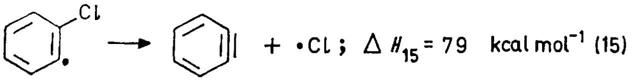
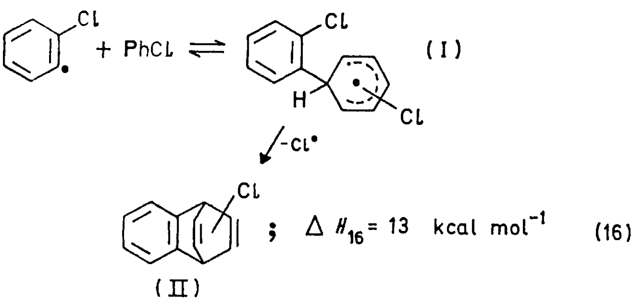
[11] S. W. Benson and R. Shaw, *J. Chem. Phys.*, 1967, **47**, 4052.
[12] M. C. Sauer, jun., and I. Mani, *J. Phys. Chem.*, 1970, **74**, 59.
[13] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, 1963, **85**, 1798.

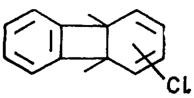
benzyne is not a likely intermediate for the production of the small amount of (chloro)naphthalene in the pyrolysis of chlorobenzene.

The current value for $\Delta H^0{}_f(C_6H_4)_g$, *ca.* 118 kcal mol^{-1},[14] leads to ΔH_{14} *ca.* 85. As the activation energy for step (—14) will be at least several kcal mol^{-1}, a reasonable estimate would seem $\log k_{14} = 13 - 90/2{\cdot}303RT$. With these parameters, with a residence time of 24 s and for 0·5% of reaction (conditions of ref. 3) the temperature to match is estimated to be 900° rather than 690°.

We have considered o-$\cdot C_6H_4Cl$ radicals as alternative precursors for naphthalene. Indeed, thermolysis of the allyl ester of *ortho*-chlorobenzoic acid in an excess of chlorobenzene at *ca.* 500° leads to *ortho*-chlorobiphenyl (without any *m*- or *p*-isomer) and naphthalene (*ca.* 1 : 1); the product ratio appears to be fairly constant with temperature (480—530°). We reject step (15) as this reaction will be too slow in order to compete noticeably with reactions (8) and (9). We suggest that compounds (I) and (II) are the intermediates, as seen in reaction (16); * (II) is thought to arise from (I) through intramolecular replacement of *ortho*-Cl.† Adducts such as (II) are known[13] to lose acetylene yielding naphthalene derivatives at elevated temperatures. In order to obtain more insight in this area reactions with other *ortho*-substituted phenyl radicals o-$ZC_6H_4\cdot$, involving substituents with different Z–Ph bond strengths, have to be considered.





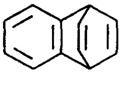


(III)

APPENDIX

Thermochemical and Kinetic Data.—Heats of formation (kcal mol^{-1}), entropy (cal mol^{-1} K^{-1}), and kinetic data are abstracted from standard compilations.[15]

For reaction (1), $\Delta H_1 = 91{\cdot}5$, taking $\Delta H^0{}_f(Ph\cdot)_g = 75$ [*i.e.*, $D(Ph\text{–}H) = 109$; [5,16] $S^0{}_1 = 34$ (unit pressure), or $+12$ (unit concentration, mol ml^{-1}, 500°). With $\Delta S_1{}^‡ = +12$ (maximum value), $\log (A_1/s^{-1}) = 16{\cdot}4$. We favour $\log A_1 = 15$, implying $\log A_{-1}$ *ca.* 12·5.



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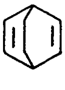

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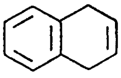

(VII)

For reaction (2) with $D(H\text{–}C_6H_4Cl) = 109$, $\Delta H_{2,-2} = 6$. Our choice for $E_2 = 8$ implies $E_{-2} = 2$, *i.e.* a little less than the activation energy for $\cdot Me + HCl$ (3 kcal mol^{-1}).[17]

For reaction (3) see ref. 1.

Reaction (4) in contrast with reaction (3) is an irreversible process; $\log A_4$ is as expected for this type of reaction; [15d] furthermore, parameters are adjusted so as to make $k_4/k_{3\,\text{eff}} = 0{\cdot}1$.

For reactions (5)—(7), supposing $E_5 = E_6$, one arrives at E_{-5} *ca.* 15; this value is, of course, much larger than that for the 'real' process $Ph\cdot + HCl \longrightarrow PhH + \cdot Cl$, which may well be below 5 kcal mol^{-1}.[18] Reaction (7) is markedly endothermic; E_{-7} is at least 6; [18] therefore, $k_7 \ll k_5, k_6$.

The parameters for reactions (8) and (9) are thought to be almost identical to those of reactions (3) and (4).

For reaction (15), with gaseous heats of formation PhCl 12, benzyne 118, •Cl 29, and $D(o\text{-}ClC_6H_4\text{–}H) = 108$, one obtains $\Delta H^0{}_f\ (o\text{-}ClC_6H_4\cdot) = 68$. Hence, $\Delta H_{15} = 79$ kcal mol^{-1}.

For reaction (16) (a) the heat of formation for compound (IV), the parent hydrocarbon of (II), is estimated as follows: (i) $\Delta H^0{}_f(V)_g$ is calculated as 38 kcal mol^{-1} *via*-$\Delta H^0{}_f(VI)_g = -6$, an estimated heat of sublimation (15 kcal mol^{-1}) and adding $+29$ as the increment for $\text{–}CH_2\text{–}CH_2\text{–} \longrightarrow \text{–}CH\text{=}CH\text{–}$; and (ii) from $\Delta H^0{}_f(\text{cyclohexene})_g = -1$ and $\Delta H^0{}_f(VII)_g = 33$, the 'benzo' increment is $+34$. Hence, $\Delta H^0{}_f(IV)_g = 38 + 34 = 72$; the uncertainty is, of course, several kcal mol^{-1}. (b) For the model reaction $o\text{-}ClC_6H_4\cdot + PhH \longrightarrow\longrightarrow (IV) + \cdot Cl$ current data [*cf.* also reaction (15)] lead to $\Delta H = 13$.

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* Other reactions involving allyl *o*-chlorobenzoate (with estimated $\Delta H^0{}_f - 59$ kcal mol^{-1}) are considered unlikely. Thus, direct splitting into benzene, CO_2, and allyl chloride is endothermic by no less than 83 kcal mol^{-1}; the radical $o\text{-}(C_3H_5OCO)\text{-}C_6H_4\cdot$ ($\Delta H^0{}_f$ *ca.* 2) would need at least 63 kcal mol^{-1} for splitting off benzyne.

† 1,2-Reaction may give compound (III) as an intermediate. By loss of hydrogen biphenylene may arise. *via* Molecular rearrangement it may also produce naphthalene.

[14] H.-F. Grützmacher and J. Lohmann, *Annalen*, 1967, **705**, 81.

[15] (*a*) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279; (*b*) D. R. Stull, E. F. Westrum, jun., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969; (*c*) J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970; (*d*) S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968.

[16] G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2077; T. Bercés, F. Màrta, and I. Szilágyi, *J.C.S. Faraday I*, 1972, **68**, 867.

[17] M. L. Poutsma, *Methods Free Radical Chem.*, 1969, **1**, 79.

[18] A. F. Trotman-Dickenson, *Adv. Free Radical Chem.*, 1965, **1**, 1.

EXPERIMENTAL (With H. P. VAN KEULEN)

Methods.—For a description of the apparatus and techniques, see ref. 6. M.p.s and b.p.s are uncorrected. Analyses were performed by gas chromatography, using mixtures of known composition for calibration purposes. Carbon monoxide was detected on molecular sieves 5 A at 70° with nitrogen (carrier gas in vapour phase runs) serving as internal standard. Benzene and chlorobenzene were separated on Carbowax at 100°, Porapak at 200°, or TECEP at 105°. (Chloro)biphenyls were separated on Bentone–SE30 at 180°. Mass spectral analyses were performed by A.E.I. Ltd., Manchester.

Materials.—Benzene, chlorobenzene, and *ortho*-dichlorobenzene (high grade commercial products) were fractionated before use, middle cuts only being employed. Commercial trioxan, azobenzene, biphenyl, and naphthalene were recrystallised to give samples of high purity. Tank chlorine (Loosco) was used as such. The allyl esters of *o*-, *m*-, and *p*-chlorobenzoic acid were synthesised *via* the acid chlorides according to the procedure described for allyl benzoate;[10] *ortho*-, b.p. 130° at 16 mmHg; *meta*-, b.p. 143—145° at 29 mmHg, n_D^{20} 1·5316; *para*-, b.p. 137° at 19 mmHg, n_D^{20} 1·5360. *p,p'*-Dichloroazobenzene was formed by the reaction of *p*-chloroaniline and *p*-chloronitrosobenzene[19] in acetic acid at 20° for 24 h. After recrystallisation from ethanol, it had m.p. 184—185°. *ortho*-, *meta*- and *para*-Chlorobiphenyl were formed by diazotisation of the corresponding chloroaniline and treatment with benzene and aqueous alkali. Work-up, distillation, and recrystallisation led to reference materials of adequate purity (g.l.c.); *ortho*-, m.p. 31—31·5°; *para*-, m.p. 75·7—76·3°; *meta*-, b.p. 158—160° at 20 mmHg, n_D^{20} 1·6201. Bichlorophenyls were prepared in mixtures of three at a time from *o*-, *m*-, or *p*-chloroaniline and chlorobenzene as described above for PhC_6H_4Cl. Biaryl fractions were redistilled twice, giving yellowish oils (*ca.* 20%), b.p. 275—320°. With these mixtures individual isomers can be unambiguously identified by g.l.c. Pure *p,p'*-$ClC_6H_4{\cdot}C_6H_4Cl$ was made from benzidine *via* double diazotation and treatment with a solution of CuCl in aqueous HCl. Work-up and distillation (*ca.* 315°) gave *material* (55%) with m.p. 145—146° (Found: Cl, 31·2. $C_{12}H_8Cl_2$ requires Cl, 31·7%). G.l.c. showed 2% *para*-PhC_6H_4Cl as the only contaminant.

[2/2408 *Received*, 23*rd October*, 1972]

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[19] *Org. Synth.*, 1955, **3**, 668.