Vapour-phase Chemistry of Arenes. Part 3.† Vapour-phase Chlorination of Benzene Derivatives catalysed by Ultraviolet Light

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The thermal, vapour-phase chlorination of benzene derivatives above *ca.* 300° can be greatly enhanced by u.v. light. A number of examples (105—245°) are given. The main features, relative rates, and isomer patterns remain unchanged. Apparently, the u.v. light is only operative in dissociating chlorine molecules, product-forming steps being the same in the two systems. In the photolytic process substantial proportions of highly chlorinated biaryls are also produced. These products are rationalized as being formed *via* dimerisation of cyclohexadienyl radicals produced by reversible addition of Cl• to arene. This interpretation is corroborated by a thermochemical–kinetic analysis. Performing the chlorination by illuminating the vapours of a refluxing arene, with recycling, monochlorinated products are obtained in high yields, rendering this simple technique the preferred synthetic method for a number of cases.

BENZENE and derivatives, upon treatment with molecular chlorine in the vapour phase, lead to chlorinated products according to equation (1).[1] The thermal,

$$\mathrm{ArH} + \mathrm{Cl_2} \longrightarrow \mathrm{ArCl} + \mathrm{HCl} \qquad (1)$$

uncatalysed reaction, when conducted in a flow system operating at atmospheric pressure, sets in at *ca.* 300°, at residence times (t) of 1—3 min.[1] The reaction is slower by at least an order of magnitude than the free-radical chlorination of aliphatic substrates such as methane or chloroform. The reaction rate is markedly enhanced when small proportions of bistrichloromethyl sulphone (S) are added to the feed. For example, at 181° and $\bar{t}$ 2.5 min, an inflow of C_6H_6–Cl_2–N_2–S (molar ratio 3 : 1 : 7 : 0.03) led to 85% chlorine conversion.[2] Even in the liquid phase at 100—170°, S was capable of inducing some substitution (1).[3]

This aromatic substitution process shows a unique pattern of isomer distribution: ‡ 'electrophilic' substrate reactivity is accompanied by 'nucleophilic' *meta* : *para* isomer ratios throughout.[1] This has tentatively been interpreted by a free-radical chain mechanism with (2) and (3) as chain-carrying steps.[3] As (2) is markedly endothermal (the C–H bond strength in

$$\mathrm{ArH} + \mathrm{Cl}\cdot \longrightarrow \mathrm{Ar}\cdot + \mathrm{HCl} \qquad (2)$$

$$\mathrm{Ar}\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{ArCl} + \mathrm{Cl}\cdot \qquad (3)$$

benzene is *ca.* 109 kcal mol^{-1} [4]) its transition state is 'late' according to the Hammond postulate. Hence, relative rates for hydrogen abstraction will reflect substituent effects on the stability of the final state (Ar•) rather than on the initial state (ArH).

The catalytic effect of added S is explained through its thermolysis to give $Cl_3C\cdot$ radicals, which rapidly react with Cl_2 to yield chlorine atoms capable of initiating reaction (1) *via* (2).[3] We now report that reaction (1) can be made to occur smoothly at temperatures even as low as 100° when conducting the vapour phase reaction under the influence of u.v. light. Using a modified reactor, selective monosubstitution can easily be achieved.

RESULTS AND DISCUSSION

Four benzene derivatives C_6H_5Z (Z = F, Cl, CF_3, and CN) have been chlorinated using the Pyrex flow reactor system depicted in Figure 1.

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† Part 2, R. Louw, J. W. Rothuizen, and R. C. C. Wegman, *J.C.S. Perkin II*, 1973, 1635.

‡ Vapour-phase bromination leads to essentially the same isomer distributions (m : p ratios).[1a]

[1] (*a*) E. C. Kooyman, *J. Pure Appl. Chem.*, 1963, **7**, 193; (*b*) 'Advances in Free-Radical Chemistry,' ed. G. H. Williams, Logos Press, London, 1965, ch. 4; (*c*) C. A. de Mey and E. C. Kooyman, *Rec. Trav. chim.*, 1971, **90**, 1337.

[2] W. Dorrepaal and R. Louw, *Rec. Trav. chim.*, 1971, **90**, 700.

[3] R. Louw, G. in't Veld, and W. Dorrepaal, *J.C.S. Perkin II*, 1973, 650.

[4] (*a*) G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc* 1971, **67**, 2077; (*b*) R. Louw and W. Dorrepaal, *Internat. J. Chem. Kinetics*, submitted for publication.

At 120 ± 20° and $\bar{t}$ *ca.* 5 min, using $C_6H_5Z : Cl_2$ intake ratios of 3 ± 1, chlorine conversions were from 10 to 40%. The isomer distributions of ZC_6H_4Cl, determined by g.l.c., are compared with those for *S*-catalysed chlorination at *ca.* 185°, and with those for the purely thermal reaction at *ca.* 300° (Table 1). These data leave little doubt that, basically, the same mechanism is operative. The small, but distinct trends in the isomer ratios for each substrate are considered to be a temperature effect. From *o* : *m* and/or *o* : *p* ratios it can be seen that substitution at *ortho*-positions is 1—2 kcal mol^{-1} higher in activation energy than at *meta* or *para*. This can be rationalized on steric grounds. Note also that the 'nucleophilic' *m* : *p* ratios (2.7 ± 0.5 for Z = F or Cl, and 1.5 ± 0.2 for Z = CF_3 or CN) tend to the statistical factor of 2 with increasing temperature.

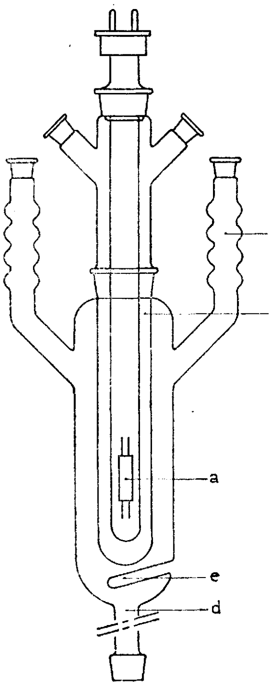


FIGURE 1 Flow-type reactor (750 ml): a, Hanau TQ 81 lamp; b, cooling mantle; c, inlet tube–preheating zone; d, outlet tube; e, thermocouple well

TABLE 1

Isomer distributions [*o* : *m* : *p* (%)] for vapour-phase chlorination of C_6H_5Z under different conditions

Method [a]	*t*/°C	Z: F	Cl	CF_3	CN
U.v.	105	2.5 : 74.5 : 23.0	6.8 : 68.5 : 24.7	5.9 : 57.9 : 36.2	
	132			6.8 : 57.3 : 35.9	6.4 : 54.0 : 39.6
S	185	2.9 : 71.7 : 25.4	9.0 : 67.0 : 24.0	6.4 : 58.1 : 35.5	7.8 : 55.1 : 37.1
Δ	300	6.5 : 65.5 : 28.0	12.3 : 61.1 : 26.6	10.4 : 56.9 : 32.7	11.8 : 53.5 : 35.2

[a] U.v. = using u.v. light (Pyrex filter); *S* = catalysed by $CCl_3SO_2CCl_3$; Δ = thermal chlorination.

Competitive chlorination of benzene *versus* fluorobenzene shows a similar trend, the relative rate decreasing from 7.8 (100°; photochemical) *via* 6.4 (185°; *S*-catalysed [2]) to 5.6 (300°; thermal reaction).

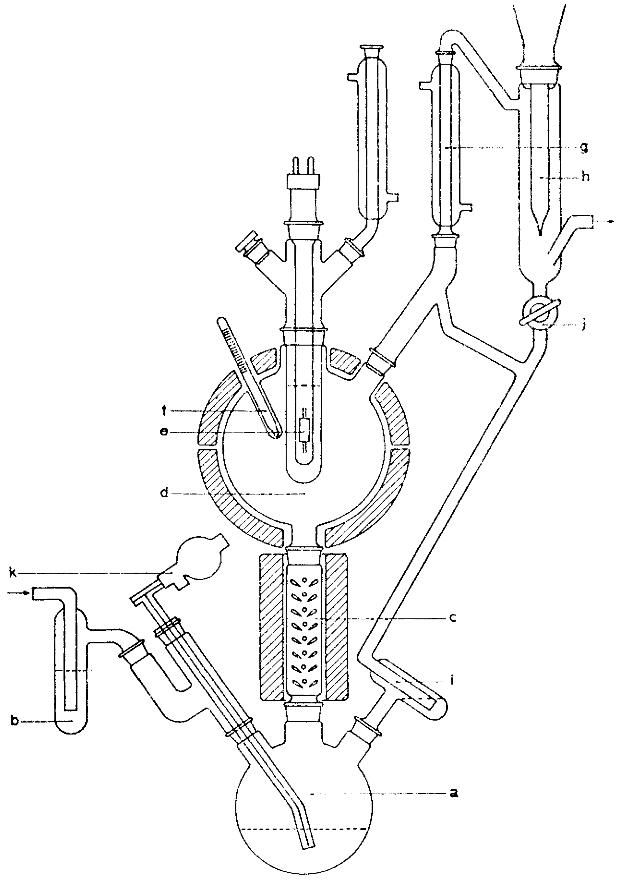


FIGURE 2 Preparative scale reactor system: a, 250 ml flask; b, chlorine inlet; c, Vigreux column; d, thermally isolated reaction chamber; e, Hanau TQ 81 lamp; f, thermometer; g, condenser; h, cold finger (ice or dry ice, optional); i, liquid valve; j, stopcock; k, sampling

Fluorobenzene is about as reactive as chlorobenzene. Although replacement of H by Cl thus has a marked deactivating effect (note the 'electrophilic' character of the intermolecular competition), further chlorination cannot be prevented when allowing larger degrees of conversion $C_6H_5Z \longrightarrow ZC_6H_4Cl$.*

A satisfactory preparation of monochlorinated products is possible only when recycling is applied. Therefore, we also used the gas-phase reactor outlined in Figure 2, enabling chlorination of the vapour of a

* For example, in a competitive run (at 109° and $\bar{t}$ 5 min) of benzene (1 mol) with fluorobenzene (2.1 mol) and Cl_2 (1.2 mol), chlorine conversion being 63%, 0.41 mol of chlorobenzene and 0.048 mol of $C_6H_4Cl_2$ were formed. From these data a relative rate for benzene *versus* chlorobenzene of *ca.* 9 is derived.

refluxing arene. Representative data are collected in Table 2. Clearly, high yields of ArCl can be obtained in this way. Correcting for the small amounts of unconverted starting arene, selectivities of 80—90% are achieved. This method may therefore be of synthetic value in a number of cases.*

TABLE 2

Preparative-scale monochlorinations [a]

Substrate (g)	Duration (h)	T/°C	Product composition (g)			
			ArH	ArCl	$ArCl_2$	Residue
$C_6H_5CF_3$ (45.2)	4	180	6.2	40.7	5.1	39.9 [c]
C_6H_5CN (49.6)	10	245 [b]	13.7	41.8	2.0	4.5 [d]
o-$C_6H_4Cl_2$ (52.5)	7	240	8.9	40.8 [f]	3.3	10.2 [e]

[a] A stream of Cl_2 (0.2 mol h^{-1}) was passed through. [b] The u.v. lamp was cooled, and the light filtered, by liquid biphenyl; in the other cases a stream of air was used. [c] Cl, 30.86% [$(C_6H_{0.3}Cl_{3.7}CF_3)_2$]. [d] Cl, 23·54% [$(C_6H_{2.25}Cl_{1.75}CN)_2$]. [e] Cl, 54.84% [$(C_6H_{1.05}Cl_{3.95})_2$]. [f] 22.8% 1,2,3-$C_6H_3Cl_3$; 77.2% 1,2,4-$C_6H_3Cl_3$.

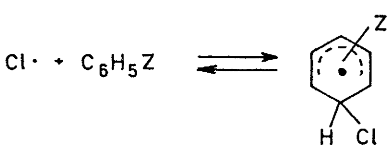
Note that the reaction proceeds well when filtering the light, not only by Pyrex glass, but also by liquid arene. Analogous observations have been made for the chlorination of fluorobenzene, refluxing benzene serving as filter and coolant. Therefore, it can safely be assumed that the light is serving rather for dissociation of chlorine than for activation of the arene; there is no reason for assuming a 'photosubstitution' mechanism[5] involving excited states of aromatic substrates.

Higher boiling products were also formed. These materials, upon analysis by i.r. and mass spectrometry, were found to consist chiefly of polychlorinated biphenyls. On the basis of elementary analysis (chlorine content) overall compositions show that little hydrogen is left unsubstituted.

These facts contrast with (earlier) observations for thermal chlorination at 300—400°. Even at complete chlorine conversion, only minor amounts of biaryl are formed in these reactions. Using CCl_4 rather than Cl_2 as 'chlorinating' agent, biaryl is the major product, however.[6] In both cases aryl radicals, formed *via* reaction (2), will lead to biaryl *via* homolytic arylation (4) (*cf.* arene pyrolysis[7]).

Reaction (4) is much slower than (3). In the present case, using a rather high Cl_2 : arene intake ratio and with partial chlorine conversion only, such a mode of formation of biaryl appears to be highly unlikely. A more logical interpretation of the formation of (polychloro)-biaryl is that *via* reversible addition of Cl· to ArH [reaction (5)],† adduct cyclohexadienyl type radicals A· dimerizing [reaction (6)], dicyclohexadienes A_2 subsequently being converted into biphenyl derivatives.‡ Thus (6) constitutes part of the termination process in the u.v. light-catalysed chlorination. Roughly speaking, at *ca.* 200°, *ca.* 20 moles of ArCl appear to be formed [reactions (2) and (3)] per equivalent of A_2 [reaction (6)].

$$\text{Ar}\cdot + \text{ArH} \xrightarrow{(-\text{H}\cdot)} \text{Ar-Ar} \qquad (4)$$



(A·) (5)

$$2\text{A}\cdot \longrightarrow \text{A}_2 \quad \left[\xrightarrow{\text{Cl}_2} \text{polychlorobiaryls} \quad (6) \right]$$

This interpretation can be supported by considering the (relative) rates of individual steps on the basis of known thermochemical–kinetic data.

From Table 2 one derives a rate of chlorination of *ca.* 10^{-5} § at 200°. Using the value for k_2 for benzene[3] of $\log k_2 = 10 - 8/2.303RT = 6.2$ (200°), $\log k_2$ for the slower reacting benzonitrile is *ca.* 5.5. With $[Cl_2] \approx [ArH] = 0.5$ atm. or *ca.* 10^{-2}M, the overall rate $R_2 = k_2[ArH][Cl\cdot] = 10^{-5}$ leads to $\log[Cl\cdot]$ *ca.* -8.5. For $R_2 : R_6 = 20$, $\log R_6 = -6.3$. Taking a normal value for $\log k_6$, *viz.* 9, $\log[A\cdot]$ becomes *ca.* -7.6. In other words, $[A\cdot] : [Cl\cdot]$ is *ca.* 10. This figure is in satisfactory agreement with the value derived from thermochemical data.¶

Under these conditions, with $[A\cdot] : [Cl\cdot] \geqslant 10$, other termination steps are relatively unimportant, and, therefore, do not significantly contribute to the formation of ArCl. R_7 will, at best, be the same as R_6,[10] whereas R_8 is an order of magnitude slower than R_6, due to the lower [Cl·] compared with [A·]. Note that recombination of chlorine atoms (9) is *not* fast compared

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* *E.g.*, substrates which cannot be chlorinated in the usual way (such as aryl cyanides), and those for which a useful isomer pattern obtains [*e.g.* p-$C_6H_4F_2$ or p-$C_6H_4(CN)_2$ to give one monochloride].

† This step would not lead to chlorinated product ArCl to a substantial degree. (At lower temperatures, in the liquid phase, A· is the precursor for the products of *additive* chlorination).[3]

‡ The latter process can be rationalized *via* addition of Cl_2 to A_2 and analogues, giving chlorinated cyclo-hexenes (and -hexanes); this, combined with abstraction of allylic (aliphatic) hydrogen by Cl· ultimately leads to aromatization.

§ Concentrations in M, time in s, energies in kcal mol^{-1}.

¶ For $H\cdot + C_6H_6 \rightleftharpoons C_6H_7\cdot$, $\Delta H° = -29$ kcal mol^{-1}, $\Delta S° = 23$ cal mol^{-1} K^{-1}.[8,9] Accepting the same data for $H\cdot + C_5H_5Cl \rightleftharpoons (A\cdot;\ Z = H)$ one finds $\Delta H°(A\cdot;\ Z = H) = 35.5$ kcal mol^{-1}, $\Delta S°(A\cdot;\ Z = H) = 12.5$ cal mol^{-1} K^{-1}. Then, for the equilibrium $Cl\cdot + C_6H_6 \overset{K}{\rightleftharpoons} (A\cdot;\ Z = H)$, $\Delta H° = -13$ kcal mol^{-1}, $\Delta S° = +21$ cal mol^{-1} K^{-1} (entropies expressed at unit pressure), leading to $\log (K/atm^{-1}) = 1.5$ (200:); with $[C_6H_6] = 0.5$ atm, one arrives at $[(A\cdot;\ Z = H)]:[Cl\cdot]$ *ca.* 20.

[5] J. Cornelisse and E. Havinga, *Chem. Rev.*, 1975, **75**, 353.

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

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

[8] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968.

[9] For standard heats and entropies of formation, see, for example, D. R. Stull, E. F. Westrum, jun., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969.

[10] *Cf.* M. J. Perkins, *Free Radicals*, 1971, **2**, 254.

with (6). For Cl_2 as a third body, the rate constant [11] $\log k_9 = 10$ leads to $\log R_9$ *ca.* -7 (*cf.* $\log R_6$ *ca.* -6).

$$2A\cdot \longrightarrow ZC_6H_4Cl\ (+\ ZC_6H_6Cl) \qquad (7)$$

$$A\cdot + Cl\cdot \longrightarrow ZC_6H_4Cl + HCl \qquad (8)$$

$$Cl\cdot + Cl\cdot\ (+\ M) \longrightarrow Cl_2\ (+\ M) \qquad (9)$$

At increasing temperatures, with increasing [Cl•] : [A•] ratio, reaction (9) will become progressively important. For the thermal chlorination, having the 'slow' initiation reaction (−9), termination will proceed largely, if not completely, *via* reaction (9). An account of the kinetics and mechanism of the latter process is given elsewhere.[4b]

EXPERIMENTAL

Apparatus and methods have been described before.[2,3,7] Mass spectra were recorded by Dr. J. van Thuyl, Dr. K. J. Klebe, and J. J. van Houte on an A.E.I. MS902 instrument. Elemental analyses were performed at the Institute for Organic Chemistry TNO, Utrecht, headed by Mr. W. J. Buis.

Chemicals.—All starting materials, as well as the chlorinated derivatives described were commercial products of adequate purity; *m*-ClC_6H_4CN was made by standard procedures.

Analyses by g.l.c. were performed on a Becker Multigraph F 410 (flame ionization detector) and/or an (isothermal) Becker 7020 instrument equipped with a katharometer system. Generally, Benton–SE (5% w/w) on Embacel 80—100 mesh, was employed. Quantitative determinations were made using standard mixtures of reference materials.

Residual materials from preparative-scale runs were obtained after distillation of more volatile products *in vacuo* at 0.3 mmHg (up to 30° for $C_6H_5CF_3$, and 180° for C_6H_5CN and *o*-$C_6H_4Cl_2$). Analyses were made by mass spectrometry, by i.r. spectroscopy, and for Cl content. The residues were shown to be polychlorinated biaryls.

Representative Flow-type Run (cf. *Figure* 1).—This reactor is mounted in an electric furnace and further operated as described for thermal gas-phase reactions.[7] A feed consisting of $C_6H_5CF_3$ (48.9 mmol h^{-1}), Cl_2 (22.6 mmol h^{-1}; other inlet) and nitrogen (174 mmol h^{-1}; both inlets) was used. After starting the illumination and equilibrating the temperature (132°), two samples were withdrawn (after 1 and 1.5 h, respectively) by freezing into a cold trap (−76°) during 15 min. Work-up was through addition of aqueous alkali, warming to room temperature, washing, and drying. Samples were analysed (Becker 7020; 110°; H_2 0.55 atm.) using $C_6H_5CF_3$ as the internal standard.

[6/105 *Received*, 16*th January*, 1976]

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[11] A. C. Lloyd, *Internat. J. Chem. Kinetics*, 1973, **3**, 39.