

The Side-Chain Halogenation of Methylbenzenes via Electrophilic Nuclear Attack. IV. Product Analysis, Kinetics, and Mechanism of the Chlorination of Some Hexasubstituted Benzenes¹

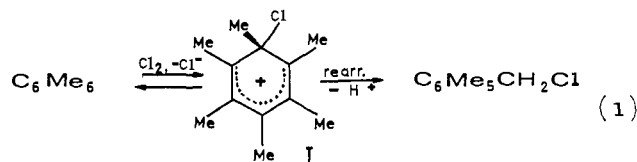
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An additional body of information concerning the electrophilic mechanism of the uncatalyzed chlorination of some hexasubstituted methylbenzenes is reported. It includes the kinetic form, the activation parameters, the selectivity of reaction, and the effects of solvents, added solutes, and light on both reaction rate and product composition. All the available data support the mechanism outlined in eq. 1 for the so-called side-chain chlorination of methylbenzenes in acetic acid, whereby a nuclear attack, and presumably the formation of a benzenonium ion, essentially control the over-all rate of reaction. Careful studies of the composition of the product under varying conditions indicate an intramolecular mechanism for the subsequent rearrangement step. Alternative, detailed mechanisms, which are briefly discussed, are possible with the data at hand. Some of the data herein reported indicate that there are conditions for the side-chain chlorination of methylbenzenes to proceed via an electrophilic nuclear attack in the nonhydroxylic, less polar solvent, carbon tetrachloride.

Introduction

We have already shown² that the uncatalyzed chlorination of hexasubstituted methylbenzenes in acetic acid solution proceeds essentially by the following steps (eq. 1). The reaction can, therefore, be regarded as a



special case of aromatic substitution whereby the final product results from rearrangement of the attacking reagent from nucleus to side chain.

The scope of this mechanism with respect to the nature of the substrate, reactant, and experimental conditions is being elucidated by our continued interest in the field. Extensions to the bromination of hexamethylbenzene and to the chlorination of trialkylbenzenes have been presented recently.³ It is also rewarding that our basic idea underlying mechanism 1 has been successfully utilized by other authors⁴ in the case

of the iodination of hexamethylbenzene by ICl in carbon tetrachloride solution.

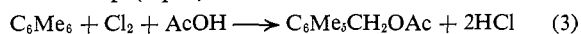
In this paper we wish to report further work on the chlorination of hexasubstituted methylbenzenes to show a more complete picture of the evidence supporting the first step of eq. 1 and some evidence concerning the rearrangement step.

Results

Product Analysis. Hexamethylbenzene reacts very rapidly with chlorine in anhydrous acetic acid in the dark. An equimolecular amount of chlorine is completely used up upon mixing the reactants in the concentration range of 0.02 to 0.05 M at room temperature. Under these conditions less than half of the halogen used up (45%) is found in the organic product and is identified as "side-chain" chlorine. The remainder (55%) is found in the solution as hydrogen chloride. Accordingly, the main over-all reaction is as follows.



The uneven distribution of the halogen between the aralkyl chloride and hydrogen chloride is due to accompanying solvolysis which amounts to 5% of the halogen used up (eq. 3). Blank runs with an authentic



specimen of chloromethylpentamethylbenzene show that solvolysis is *not* subsequent to the formation of the aralkyl chloride. The extent of this side-reaction increases in the presence of sodium acetate; it is also likely to be affected by the nature of the substrate (C_6Me_5CN). All these results are summarized in Table I.

Table I. Distribution of Chlorine (Fraction per Mole Used) in the Reaction Products of the Chlorination of Hexasubstituted Methylbenzenes in Acetic Acid

	Substrate, M^a	AcONa, M	Chlorine in the organic product,		
			Total	Side chain	HCl
C_6Me_6 ,	3.050×10^{-2}	None	0.45 ^b	0.45 ^b	0.55
	2.062×10^{-2}	0.025			0.60
	1.984×10^{-2}	0.050		0.37	0.63
C_6Me_5CN , ^c	8.23×10^{-2}	None	0.37	0.37	0.63

^a The molarity of the substrate was in every case identical with that of chlorine. ^b Average from three determinations. ^c The blank run was not carried out in this case.

Equation 2 is an oversimplification of the over-all processes leading to products chlorinated in the side chain. Although chloromethylpentamethylbenzene is expected to be less reactive than hexamethylbenzene,

(1) Part XXI of the series: Substitution in Polymethylbenzenes.

(2) E. Baciocchi and G. Illuminati, *Tetrahedron Letters*, No. 15, 637 (1962).

(3) (a) E. Baciocchi, G. Illuminati, and F. Stegel, Special Publication No. 19, The Chemical Society, London, 1965, p. 158; (b) E. Baciocchi and G. Illuminati, *Ric. Sci. Rend.*, 7, 462 (1964); (c) G. Illuminati and F. Stegel, *ibid.*, 7, 458 (1964).

(4) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 86, 4158 (1964).

Table II. Kinetic Data for the Uncatalyzed Chlorination of Cyanopentamethylbenzene in Acetic Acid at 30°^a

Substrate, 10 ³ × <i>M</i>	Cl ₂ , 10 ³ × <i>M</i>	10 ³ × <i>k</i> ₂ , l. mole ⁻¹ sec. ⁻¹
8.593	8.593	2.78
23.61	7.897	2.61
31.31	17.78	2.51
31.31	9.00	2.53
19.87	19.87	2.74
28.57	14.83	1.06 (at 18°)

^a *E*_a = 13.3 kcal./mole; -Δ*S** = 28.4 e.u. (at 30°).

small amounts of the unreacted hydrocarbon and of polychlorinated material of the probable type C₆Me_{6-n}(CH₂Cl)_n are found in the reaction mixture.

In addition to the analytical data reported in Table I, evidence for the composition of the products was obtained for chloromethylpentamethylbenzene, pentamethylbenzyl acetate, unreacted hexamethylbenzene, and polychlorinated products with the aid of vapor phase chromatography and infrared spectroscopy.

Although chloromethylpentamethylbenzene is the major product, on a preparative scale, by-products are removed with some difficulty; nevertheless, the pure compound can be conveniently prepared by this route.

Reaction Kinetics. The chlorination of all tested members in the series C₆Me_nXY (X, Y = Me, Cl, Br, CN) was generally found to follow second-order kinetics throughout the reaction in anhydrous acetic acid in the dark. The over-all reaction order was tested in detail in the case of C₆Me₅CN. Table II reports rate constants for this substrate at various initial concentrations of both reactants. The reaction was also found to be first order with respect to chlorine by the method of initial rates.⁵ At chlorine concentrations higher than, or equal to, that of the substrate (*ca.* 10⁻² *M*), second-order plots show drifts upward toward the end of the reaction which are attributed to the ascertained formation of polychlorinated products.

Bromopentamethylbenzene shows an unusual behavior; the reaction in this case follows apparent, second-order kinetics with a rate constant value of the expected magnitude (see below) up to about 50% change but rapidly slows down henceforth. Also, in the later stages of the reaction a yellow color develops as the concentration of the halogen decreases instead of the complete discharge of the weak chlorine color as normally observed. The nature of the supervening complications with this substrate has not been investigated any further.

Energies and entropies of activation were estimated from rate data at 18 and 30° for cyanopentamethylbenzene. They are included in Table II.

In order to obtain information on the effect of the structure on the rate of side-chain chlorination, the reactivity of hexamethylbenzene was compared to that of hexasubstituted compounds in the series C₆Me_nXY. The kinetic data are collected in Table III. In view of the experimental complexity of the latter part of the reaction of C₆Me₅Br, the *k*₂ value corresponding to the linear portion of the second-order plot (up to 50% reaction) was considered in this case. The effects of

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 45.

Table III. Kinetic Data for the Uncatalyzed Chlorination of Some Hexasubstituted Benzenes in Acetic Acid^a and Comparison of Substituent Effects in Three Chlorination Reactions

Benzene derivative, C ₆ Me _n XY	X, Y	10 ⁵ × <i>k</i> ₂ , l. mole ⁻¹ sec. ⁻¹
C ₆ Me ₆	CH ₃ , CH ₃	<i>ca.</i> 3.90 × 10 ^{5b}
C ₆ Me ₅ Cl	Cl, CH ₃	1.27 × 10 ⁶
C ₆ Me ₅ Br	Br, CH ₃	7.90 × 10 ⁴
C ₆ Me ₅ CN	CN, CH ₃	2.64 × 10 ²
C ₆ Me ₄ Cl ₂ ^c	Cl, Cl	1.42 × 10
Chlorination reaction	<i>k</i> _{Me} / <i>k</i> _{Cl} ^d	<i>k</i> _{Me} / <i>k</i> _{CN} ^d
Electrophilic "side-chain" ^e	<i>ca.</i> 3 × 10 ⁸	<i>ca.</i> 1.4 × 10 ⁶
Electrophilic "nuclear" ^f	0.8 × 10 ³	12.8 × 10 ⁶
Radical "side-chain" ^g	2.2	4.3

^a At 30°. ^b At 18°. ^c 3,6-Dichlorotetramethylbenzene. ^d Relative reaction rates. ^e Data obtained from the values reported in the upper part of this table. ^f Data from the nuclear chlorination of 3-substituted durenes in acetic acid: E. Baciocchi and G. Illuminati, *Ric. Sci. Rend.*, **3**, 1127 (1963). ^g Data from the free-radical chlorination of *para*-substituted toluenes: C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957).

the halogens and of the cyano group are markedly retarding and the following reactivity order is observed: C₆Me₆ > C₆Me₅Cl, C₆Me₅Br > C₆Me₅CN > C₆Me₄Cl₂. The over-all reactivity range is covered by a kinetic factor as large as 10⁷.

When present in concentrations comparable to those of the reactants (10⁻² to 10⁻³ *M*), iodine and zinc chloride act as mild catalysts, with no apparent modification of the reaction order in the reactants. A fairly large concentration (10⁻¹ *M*) of lithium chloride gives rise to but a slight rate increase.

The effect of increasing concentrations of water (from 1.9 to 4.1 *M*) is found to enhance the reaction rate to substantial factors (from 10 to 30). Water may somewhat modify the kinetic course of the reaction, since second-order plots show marked upward drifts. No kinetic effect was observed on addition of *p*-cresol (10⁻⁴ *M*). Catalyst and medium effects are summarized in Table IV.

Some solvent and light effects are shown in Table V. The rates of uncatalyzed chlorination are greatly affected by the nature of the solvent, the hydroxylic acid being much "faster" solvent than the less polar, aprotic carbon tetrachloride.

The effect of light is a complex one, for it depends on the solvent as well as on the substrate. Thus the reaction rate of chloropentamethylbenzene is strongly accelerated by light in carbon tetrachloride and is unaffected in acetic acid; that of hexamethylbenzene is weakly accelerated in carbon tetrachloride and is presumably unaffected in acetic acid. The implications of these phenomena on the reaction mechanism are discussed in the next section.

Discussion

One group of the results described in the preceding section confirms and adds new evidence to the view² that the first step of the reaction consists of an electrophilic attack of molecular chlorine on the aromatic ring to form the benzenonium ion I, as shown in eq. 1. This conclusion follows from the fact that these results are in close analogy with the corresponding properties known for electrophilic aromatic chlorination and in marked contrast with those expected from a direct,

Table IV. Catalyst and Medium Effects on the Rate of the Uncatalyzed Chlorination of Hexasubstituted Methylbenzenes in AcOH at 30°

Substrate, <i>M</i>	Cl ₂ , <i>M</i>	Added substance, <i>M</i>	<i>k</i> ₂ , l. mole ⁻¹ sec. ⁻¹	<i>k</i> _{aqAcOH} / <i>k</i> _{AcOH}
C ₆ Me ₅ CN				
9.910 × 10 ⁻³	6.515 × 10 ⁻³	ZnCl ₂ , 4.515 × 10 ⁻²	7.11 × 10 ⁻³	
1.097 × 10 ⁻²	1.097 × 10 ⁻²	I ₂ , 1.065 × 10 ⁻³	9.32 × 10 ⁻³	
8.590 × 10 ⁻³	8.590 × 10 ⁻³	None	2.64 × 10 ⁻³	1
1.190 × 10 ⁻²	1.190 × 10 ⁻²	H ₂ O, 1.87	2.86 × 10 ⁻²	10.8
1.160 × 10 ⁻²	5.790 × 10 ⁻³	3.08	4.93 × 10 ⁻²	18.7
1.170 × 10 ⁻²	5.870 × 10 ⁻³	4.10	7.34 × 10 ⁻²	27.8
C ₆ Me ₅ Cl				
4.85 × 10 ⁻³	4.85 × 10 ⁻³	<i>p</i> -Cresol, 9.69 × 10 ⁻⁵	1.27	
8.50 × 10 ⁻³	8.50 × 10 ⁻³	LiCl, 0.10	1.55	

Table V. The Effect of Light on the Rate of Chlorination of Hexasubstituted Methylbenzenes at 30°

Substrate and solvent	Reaction rates		Accel- eration by light	Probable mechanism under illumination
	Dark	Light		
C ₆ Me ₅ Cl, AcOH	1.27 ^a	1.28 ^a	None	SE
C ₆ Me ₅ Cl, CCl ₄	1850 (6%) ^b	12 (50%) ^b	Large	SR
C ₆ Me ₆ , CCl ₄	24 (50%) ^b	5.6 (50%) ^b	Small	SR and SE
Substituent effect in CCl ₄ : Me vs. Cl	2000 ^c	2 ^c		

^a Second-order rate constants in l. mole⁻¹ sec.⁻¹. ^b Time at a given per cent of reaction (shown in parentheses), in minutes; the molarity was 0.015 in both reactants. ^c Rate for C₆Me₆ relative to C₆Me₅Cl (based on times at 6% reaction).

free-radical attack at the side chain. All the available evidence in this connection is summarized in the following. (a) In anhydrous acetic acid solution the kinetic form of the reaction is rate = *k*[substrate][Cl₂]. (b) The activation parameters obtained for cyanopentamethylbenzene (Table II) fall in the range found for the nuclear chlorination of several methylbenzenes⁶ (*E*_a, 7 to 12 kcal./mole; -Δ*S*^{*}, 13 to 35 e.u.). (c) The substituent effects, as expressed in terms of *k*_{Me}/*k*_{Cl} and *k*_{Me}/*k*_{CN} reactivity ratios, show that this reaction is a highly selective one. Data for comparison with other reactions are reported in Table III to illustrate that such a selectivity is very similar to that found in the aromatic chlorination of related compounds, and much higher than that found in free-radical chlorination. Also, the high absolute reactivity of hexamethylbenzene is in contrast with a free-radical attack⁷ under the conditions of these investigations, and is equally significant from the point of view of the type of reagent involved. (d) The magnitude of the effects of added ZnCl₂, I₂, and water is also similar to that found in nuclear chlorination. In particular, a water concentration as high as 4.1 *M* increases the rate of nuclear chlorination of benzene and toluene by factors of 20 to 40 as estimated from data by Stock and Himoe.⁸ In similar conditions, the rate factor for the present reaction is *ca.* 28 (cyanopentamethylbenzene, Table IV). (e) The lack of any influence of light in acetic acid solution on both kinetic form and rate constant is in complete accord with a heterolytic mechanism in this solvent.

According to eq. 1, the reaction is made of two main steps. On the basis of the above evidence, in acetic

acid solution the first step is also likely to control the rate of the whole process.

It is of interest to note, on the basis of the results reported in Table V, that in carbon tetrachloride solution the reaction probably proceeds *via* an electrophilic mechanism in the dark, as shown by a substituent effect (Me vs. Cl), but is generally subject to competition by the electrophilic and the free-radical mechanisms under illumination. In carbon tetrachloride substrates with higher aromatic reactivity (hexamethylbenzene) are more likely to react predominantly by the former mechanism (small effect of illumination), while those with lower aromatic reactivity would react predominantly by the latter (large effect of illumination). This interpretation throws light on an early observation⁹ on the occurrence of side-chain chlorination of pentamethylbenzene in this particular solvent.

Another group of results in this paper has a bearing on the rearrangement step. Some of the data suggest that the rearrangement of chlorine from nucleus to side chain is essentially intramolecular. The main evidence is provided by the limited extent of solvolysis occurring during the reaction. In electrophilic side-chain bromination^{3b} the extent of solvolysis is even more limited (in fact, no side reaction of this kind could be detected), in spite of the fact that bromine is a better leaving group than chlorine and in accordance with the fact that bromine has more tendency to form bridged compounds.¹⁰ The observation that added lithium chloride has no influence on the reaction rate is equally (thus not unequivocally) consistent with the view that the rearrangement step is not rate determining and is intramolecular.

(6) E. Baciocchi, *Ric. Sci. Rend.*, **3**, 1121 (1963).

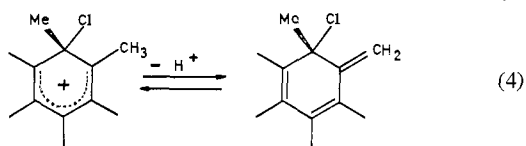
(7) See Table III, footnote *g*.

(8) L. M. Stock and A. Himoe, *J. Am. Chem. Soc.*, **83**, 1937 (1961).

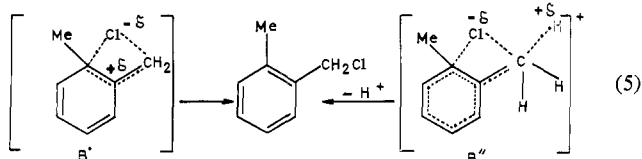
(9) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 5169 (1957).

(10) B. Capon, *Quart. Rev.*, (London), **18**, 66 (1964).

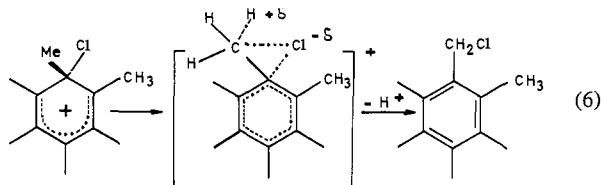
Polymethylbenzenonium ions are acidic¹¹ and may be converted to their conjugate bases, the methylene derivatives. One possible reaction path would involve a pre-equilibrium (eq. 4), followed by a sort of allylic rearrangement *via* transition state B'.



both rearrangement and proton abstraction may occur by a synchronous step *via* a transition state of type



B''. There is also a possibility for chlorine to rearrange by a 1,2-shift to the methyl carbon of the geminated position, according to path 6. The latter path



resembles a quino-benzylic rearrangement where a 1,2-shift at the geminated position of a quinohalide is a well established fact,¹² although its mechanism is not known in detail.¹³ One major driving force in all three possible reactions shown in eq. 5 and 6 rests on the rearomatization of the benzene ring. Also, in all these cases the presence of an α -hydrogen plays an essential role in the rearrangement process; accordingly, we have found independent evidence that this is so from a recent study on 1,3,5-trialkylbenzenes.^{3c}

Other reaction paths not involving intramolecular rearrangement can be devised; some of them have been mentioned previously.^{3a,3b} The evidence presented here and in other papers^{2,3b} gives experimental support to the alternative mechanisms proposed in eq. 4, 5, and 6; further work is needed to elucidate the mechanism of the rearrangement in more detail.

Experimental

Materials. Hexamethylbenzene (Eastman Kodak, reagent grade) was recrystallized from ethyl alcohol, m.p. 164.5–165°. Chloropentamethylbenzene was prepared by chlorination of pentamethylbenzene in carbon tetrachloride in the presence of iodine.¹³ The crude material was recrystallized from ethyl alcohol, m.p. 155–156°. Bromopentamethylbenzene was prepared by bromination of pentamethylbenzene in acetic acid. The melting point was 162–163° after recrystallization from ethyl alcohol (lit.¹⁴ m.p. 160°). 1,4-Dichlorodurene was obtained by chlorination of durene in acetic acid. The crude material was recrystallized

(11) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Erhart, E. F. Wadely, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(12) V. V. Ershov, A. A. Volo'dkin, and G. N. Bogdanov, *Russ. Chem. Rev.*, **59**, (1963), and references reported therein.

(13) C. Cook, N. Nash, and H. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

(14) A. Kowczynski, *Ber.*, **35**, 868 (1902).

twice from chloroform, m.p. 189–190° (lit.¹⁵ m.p. 189–190°). Cyanopentamethylbenzene was prepared according to the method of Fuson^{16,17} and purified by several recrystallizations from chloroform, m.p. 171.5–172.5°. Chloromethylpentamethylbenzene was prepared by chloromethylation of pentamethylbenzene,¹⁸ m.p. 81–83°. Pentamethylbenzyl alcohol was obtained by hydrolysis of chloromethylpentamethylbenzene in aqueous acetone, m.p. 154.5–157° after recrystallization from ethanol (lit.¹⁹ m.p. 155–158°). Pentamethylbenzyl acetate was prepared from pentamethylbenzyl alcohol and acetic acid by the standard procedure for the esterification reactions, m.p. 76.5–84.5° after two recrystallizations from ethanol (lit.¹⁹ m.p. 83–85°).

Products of the Chlorination of Hexamethylbenzene in Acetic Acid. A slightly more than equimolecular amount of chlorine dissolved in glacial acetic acid was slowly added, in the dark, to a vigorously stirred solution of hexamethylbenzene in the concentration range of 0.02–0.05 *M*. Immediately after the addition (the reaction was practically instantaneous) the acetic acid solution was poured into a two- or threefold volume of petroleum ether, b.p. 30–60°. The mixture was then washed with water until a negative chloride ion test was obtained in the aqueous layer and finally the ether layer was dried over sodium sulfate.

The crude material obtained on the evaporation of the petroleum ether was analyzed by v.p.c. with a 1-m. Dow Corning Silicone 710 column, at 190°, hydrogen being the carrier gas. The chromatogram consisted essentially of one peak with retention time corresponding exactly to that of a pure sample of chloromethylpentamethylbenzene. A very small amount of hexamethylbenzene was also detected. Since all the chlorine had been used up in the reaction, the presence of unreacted hydrocarbon was attributed to the occurrence of some polychlorination. Probably the concentration of polychlorinated materials was too low to make them detectable in the chromatogram.

The infrared spectrum also showed that the reaction product was mainly chloromethylpentamethylbenzene. However, two peaks (at 5.74 and 8.21 μ) revealed the presence of an ester²⁰ and were located at the same positions of the main absorptions of an authentic sample of pentamethylbenzyl acetate.

As expected, upon changing the order of addition of the reactants, the composition of the reaction product resulted in increased amounts of both unreacted hydrocarbon and polychlorinated materials, as was shown by v.p.c. analysis. In this case two additional peaks (dichlorinated material) were observed in the chromatogram.

It was found that pouring the reaction mixture into water followed by extraction with petroleum ether resulted in an appreciable loss of chlorinated materials; this was shown by chlorine analysis and by the isolation of a compound, insoluble in petroleum ether, which was found to be the pentamethylbenzyl alcohol (m.p. 160°).

(15) A. Tohl, *ibid.*, **25**, 1521 (1892).

(16) R. C. Fuson and J. J. Denton, *J. Am. Chem. Soc.*, **63**, 654 (1941).

(17) R. C. Fuson, W. D. Emmons, and J. P. Freman, *ibid.*, **75**, 5322 (1953).

(18) R. R. Aitken, G. M. Badger, and J. W. Cook, *J. Chem. Soc.*, 331 (1950).

(19) L. Summers, *J. Am. Chem. Soc.*, **76**, 3481 (1954).

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 178.

This compound, whose structure was confirmed by the infrared spectrum and by hydroxyl group analysis with phthalic anhydride²¹ (% OH groups found, 9.42; calcd., 9.55), must be formed by the solvolysis of chloromethylpentamethylbenzene in aqueous acetic acid which is a strong ionizing solvent. Pentamethylbenzyl alcohol was never found when the reaction mixture was first poured into petroleum ether and worked up as described in the first paragraph of this section.

Chloromethylpentamethylbenzene from Hexamethylbenzene. For synthetic purposes, an experiment was carried out with about 0.1 mole of hexamethylbenzene. An approximately 40% excess of chlorine was used in order to keep any unreacted hexamethylbenzene in the reaction product to a minimum and, therefore, to avoid troublesome separation of this high-melting hydrocarbon by fractionation from the other components of the mixture.

Owing to the low solubility of hexamethylbenzene in acetic acid, the experiment was brought about in four batches of 4 g. of hydrocarbon each by the procedure referred to above (addition of the chlorine solution into the hydrocarbon solution). The crude materials obtained from each batch were collected and were fractionated through a 90-cm. Monel spiral Todd column with total reflux and controlled takeoff at a pressure of 14 mm.

The following fractions were separated: (1) b.p. 154–159°, m.p. 85–87°, 2 g.; (2) b.p. 159–163°, m.p. 80.5–82.5°, 5.7 g.; (3) b.p. 163–190°, m.p. 65–73.5°, 2.1 g.; and (4) b.p. 186–191°, m.p. 103.5–109°, 1.5 g.

V.p.c. analysis showed that fraction 1 was mainly chloromethylpentamethylbenzene with some hexamethylbenzene and fraction 2 corresponded to chloromethylpentamethylbenzene practically pure (chlorine analysis gave 17.85% of chlorine; calcd. for chloromethylpentamethylbenzene, 18.02%). Fraction 3 again showed the peak characteristic of chloromethylpentamethylbenzene, but two other, broad-shaped peaks were also present. Fraction 4 showed the latter two peaks only. Chlorine analysis carried out on fraction 4 gave 28.75% of chlorine. Since this value is near to that expected for bischloromethyltetramethylbenzenes (32.05%), these peaks can be reasonably attributed to dichlorinated materials.

Chlorine Analysis. The crude reaction product, which was obtained as described in the preceding section, was analyzed for both side-chain and total chlorine. Side-chain chlorine analysis was carried out by the procedure described elsewhere.²² Total chlorine was analyzed by the Parr bomb method.²³

Hydrogen Chloride Analysis. In the case of the very reactive hexamethylbenzene, a solution of the compound in acetic acid was quickly added to a strongly stirred chlorine solution of known concentration. At the end of the reaction, 5.0 ml. of the mixture was added to 50 ml. of carbon tetrachloride in a separatory funnel. This solution was extracted with two 15-ml. portions of water. The aqueous layers were combined and analyzed by the Volhard method for chloride ions.

(21) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 20.

(22) E. Baciocchi and G. Illuminati, *Gazz. chim. ital.*, **92**, 89 (1960).

(23) Houben-Weyll, "Methoden der Organischen Chemie," Vol. II, George Thieme Verlag, Stuttgart, 1953, p. 41.

Table VI. Kinetic Data for the Dark Chlorination of Hexasubstituted Methylbenzenes in Acetic Acid or Carbon Tetrachloride at 30°

Aromatic compound and solvent	Time, min.	Na ₂ S ₂ O ₃ ^a , ml.	Reaction, %	log (a - x)/(b - x)	
C ₆ Me ₅ CN, AcOH: [Ar] = 3.131 × 10 ⁻² ; [Cl ₂] = 1.77 × 10 ⁻²	0	2.65	0	0.2457	
	11.5	2.52	5.08	0.2557	
	29.5	2.43	8.47	0.2628	
	70	2.00	24.67	0.3032	
	130	1.48	44.26	0.3738	
	193	1.25	52.78	0.4156	
	248	1.06	60.07	0.4632	
	293	0.91	65.72	0.5076	
	C ₆ Me ₄ Cl ₂ ^b , AcOH: [Ar] = 3.47 × 10 ⁻² ; [Cl ₂] = 1.917 × 10 ⁻²	0	8.72	0	0.25762
		807	6.86	21.33	0.30746
1419		5.91	32.25	0.34152	
2255		4.86	44.26	0.38985	
2855		4.19	51.95	0.42917	
3715		3.53	59.55	0.47731	
4290		3.17	63.65	0.50895	
C ₆ Me ₆ , CCl ₄ : [Ar] = [Cl ₂] = 1.16 × 10 ⁻²	0	4.60	0		
	13.5	3.15	31.6		
	(24)		(50) ^c		
	30.0	2.00	56.6		
	60.0	1.17	74.5		
	150	0.35	92.4		
	219	0.00	100		

^a Volumes (in ml.) of 0.01–0.025 *N* sodium thiosulfate necessary for the iodometric titration on 2-ml. samples quenched in a solution of potassium iodide in 70% ethanol for the experiments in acetic acid and of potassium iodide in 95% ethanol for the experiments in carbon tetrachloride. ^b 3,6-Dichlorodurene. ^c The value in parentheses is based upon graphic evaluation.

In the case of the less reactive cyanopentamethylbenzene, the solution of chlorine in acetic acid was added to the solution of the compound and the concentration of the chlorine was determined immediately after the addition. The reaction went to completion in 5 days. The analysis was then carried out according to the procedure described above.

Solvents. Acetic acid was purified as described elsewhere.²⁴ Carbon tetrachloride (3 kg.) was washed three times with hydroalcoholic solution of potassium hydroxide, then with water until a neutral washing was obtained. After drying over calcium sulfate for 1 day, the solvent was fractionated in a column. After a fore-run of 50 ml., 1500 ml. of carbon tetrachloride was collected at 76.5° (1 atm.).

Kinetic Procedures. Depending on the reactivity of the aromatic compounds, the procedures adopted varied somewhat from each other as described in previous papers of this series.^{22, 24} In the photochemical experiments, the reaction mixture was illuminated by a 300-w. lamp which was placed at a 2-cm. distance from the reaction flask. Typical kinetic experiments are reported in Table VI.

Infrared Spectra. The spectra were carried out with a Perkin-Elmer Model 13 spectrophotometer. In all cases a suspension of the material in Nujol was used.

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