

**Preparation of the 1-Phenylisindole-3-(N,N-diethyl)propionamide-maleic Anhydride Adduct (XIV).**—Crude XIII was prepared by treating 3 g. of XI with diethylamine, evaporating the excess diethylamine, and heating the residue to 100° under nitrogen for 24 hr. The resulting brown oil was dissolved in ether and excess maleic anhydride was added. The more maleic anhydride added the faster the crystallization of adduct, since the reaction is an equilibrium. After standing at room temperature 24 hr., 1.8 g. (44% yield) of adduct was isolated by filtration; XIV can be crystallized from benzene-hexane giving white crystals, m.p. 115–116.5°.

*Anal.* Calcd. for  $C_{25}H_{26}N_2O_4$ : C, 71.75; H, 6.26; N, 6.69; mol. wt., 418. Found: C, 71.70; H, 6.36; N, 6.76; mol. wt., 306, 265 (see text).

**Reaction of the Adduct XIV with Aniline.**—A sample of the adduct XIV was dissolved in benzene and a few drops of aniline added to give immediately a precipitate. The solution was filtered and the product washed with dilute HCl to give N-phenylmaleamic acid.

The same compound was isolated by dissolving maleic anhydride in benzene, treating with aniline, and working up in the same fashion. The two products were shown to be identical by their infrared spectra.

**Preparation of 1-Phenylisindole-1,4-naphthoquinone Adduct.**—1,4-Naphthoquinone (1 g.) was dissolved in 100 ml. of ether and this solution was added to a solution of 1 g. of 1-phenylisindole in 30 ml. of ether. After standing 24 hr. at room temperature the reaction mixture was filtered and the dark blue product recrystallized from xylene; yield 0.33 g., 16%, m.p. 222–222.5°.

*Anal.* Calcd. for  $C_{24}H_{17}NO_2$ : C, 82.03; H, 4.88; N, 3.99. Found: C, 82.26; H, 4.70; N, 3.96.

**Preparation of N-Deuterio-1-phenylisindole.**—1-Phenylisindole (0.1 g.) was dissolved in 2 ml. of dioxane, 99.8%  $D_2O$  was added to the cloud point, and the solution allowed to stand 15 min. An excess of  $D_2O$  was then added to precipitate partially deuterated 1-phenylisindole. Infrared ( $CHCl_3$ ) shows N-H at 3460 and N-D at 2560  $cm^{-1}$ .

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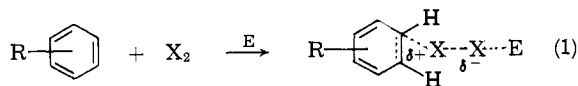
## The Electrophilic Attack of Iodine Monochloride on Hexamethyl- and Hexaethylbenzene in Carbon Tetrachloride

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Hexamethylbenzene and iodine monochloride react in carbon tetrachloride at ordinary temperatures in the dark to form pentamethylbenzyl chloride and 2 moles of iodine per mole of starting halogen. Hexaethylbenzene and iodine monochloride undergo a similar reaction. The rates of both processes are third order dependent on iodine monochloride concentration. In their kinetic aspects the reactions closely resemble the ring iodinations of mesitylene and pentamethylbenzene by iodine monochloride in carbon tetrachloride. It is concluded that the side-chain substitution products of hexamethyl- and hexaethylbenzene are formed by way of polar intermediates.

Ring halogenation of alkylbenzenes by elemental chlorine or bromine in a nonpolar medium may take place at ordinary temperatures in the presence of a polar substance E which can function as an electrophile.<sup>1</sup> It seems likely that this electrophile promotes polarization of the halogen-halogen bond by interacting with departing halide ion (eq. 1) in the activation process.



If iodine monochloride is substituted for chlorine or bromine, the halogen itself may assume the role of E.

Mesitylene and pentamethylbenzene react with iodine monochloride in carbon tetrachloride at room temperature to form, respectively, 2-iodomesitylene and 6-iodo-1,2,3,4,5-pentamethylbenzene.<sup>2</sup> Both substitution processes are third order dependent on the  $ICl$  concentration of the medium, a fact which has been tentatively explained on the assumption that the dimeric rather than the monomeric form of the polar halogen serves as the reactant E. These ring iodinations are accompanied by minor side reactions in which molecular iodine is formed. There is a growing body of evidence that under polar conditions the halogenation of alkyl-

benzenes may lead to the formation of some side-chain as well as nuclear substitution products.<sup>1b,3,4</sup> The possibility that iodine formation in the iodine monochloride reactions is associated with polar processes leading to alkyl group substitution has now been tested by investigating the products and kinetics of reaction of the mixed halogen with hexamethylbenzene and hexaethylbenzene in carbon tetrachloride. In this regard it is interesting to note that Baciocchi and Illuminati have reported that hexasubstituted alkylbenzenes are readily attacked at the alkyl side chains by chlorine in acetic acid under conditions which provide for nuclear attack on less highly alkylated benzenes.<sup>5</sup>

### Experimental

**The Kinetic Studies.**—Eastman Organic Chemicals hexamethyl- and hexaethylbenzene were used in these experiments without further purification. Spectro Grade carbon tetrachloride, also from Eastman Organic Chemicals, was stored over calcium sulfate for several days before use. The iodine monochloride was prepared from the elemental halogens.<sup>6</sup>

The rates of reaction of the aromatic hydrocarbons and iodine monochloride in carbon tetrachloride were investigated spectrophotometrically. Rate samples were stored in 1-cm. absorption cells in the temperature-controlled ( $\pm 0.1^\circ$ ) housing of a Beckman

(3) (a) R. M. Keefer, A. Ottenberg, and L. J. Andrews, *ibid.*, **78**, 255 (1956); (b) R. Josephson, R. M. Keefer, and L. J. Andrews, *ibid.*, **83**, 3562 (1961).

(4) (a) G. Illuminati and G. Marino, *ibid.*, **78**, 4975 (1956); (b) E. Baciocchi and G. Illuminati, *Gazz. chim. ital.*, **92**, 89 (1962).

(5) E. Baciocchi and G. Illuminati, *Tetrahedron Letters*, 637 (1962).

(6) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans; Green and Co., London, Eng., 1948, p. 846.

(1) (a) R. M. Keefer, J. H. Blake, and L. J. Andrews, *J. Am. Chem. Soc.*, **76**, 3062 (1954); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 5169 (1957).  
(2) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412 (1957).

spectrophotometer. In some runs with hexaethylbenzene a procedure employed previously<sup>2</sup> was used to follow the disappearance of the mixed halogen as iodine was produced. The optical densities,  $d_{450}$  and  $d_{520}$ , of the rate samples were measured from time to time both at 450 and 520  $m\mu$ , and the corresponding iodine monochloride concentrations were calculated using eq. 2 and 3.

$$d_{450} = \epsilon_{ICl}[ICl] + \epsilon_{I_2}[I_2] \quad (2)$$

$$d_{520} = \epsilon'_{ICl}[ICl] + \epsilon'_{I_2}[I_2] \quad (3)$$

In runs in which the hydrocarbon concentration was relatively small, the extinction coefficients of the two halogens were taken as equal to those in hydrocarbon-free solutions. Generally, however,  $\epsilon$  and  $\epsilon'$  values were determined separately for each reaction mixture, since they vary with changes in the structure and concentration of aromatic hydrocarbon in the medium.

It was eventually established that the reactions were essentially quantitative with respect to the conversion of two moles of ICl to one mole of  $I_2$ . For example, a mixture of initial hexaethylbenzene and iodine monochloride concentrations of 0.130 and  $9.62 \times 10^{-3} M$ , respectively, was found by spectrophotometric measurement to have an iodine concentration of  $4.60 \times 10^{-3} M$  (96% yield) when reaction was complete. Similarly, iodine was produced in 94% yield in a solution initially 0.0106  $M$  in both hexamethylbenzene and iodine monochloride. In most of the runs spectrophotometric measurements were made only at 580  $m\mu$ , a wave length at which iodine absorbs much more intensely than iodine monochloride. Equation 4, which applies when the reaction to form iodine is quantitative, was then used in calculating the corresponding ICl concentrations from the initial con-

$$[ICl] = \frac{d_{580} - [ICl]_i \epsilon''_{I_2}/2}{\epsilon''_{ICl} - \epsilon''_{I_2}/2} \quad (4)$$

centration,  $[ICl]_i$ , and the extinction coefficients,  $\epsilon''$ , of the halogens at 580  $m\mu$ .

**The Reaction Products.** (a) **From Hexamethylbenzene and ICl.**—To a solution of 3.228 g. (0.0199 mole) of iodine monochloride in 50 ml. of carbon tetrachloride was added a solution of 1.612 g. (0.00994 mole) of hexamethylbenzene in 50 ml. of the same solvent. The mixture, which almost immediately turned the deep purple color of solutions of iodine in carbon tetrachloride, was stored in the dark overnight at room temperature. The mixture was then washed with dilute aqueous sodium thiosulfate and sodium hydroxide solutions to remove iodine and hydrogen chloride. The carbon tetrachloride solution of the product was dried over calcium chloride and concentrated to dryness in a stream of air and finally under vacuum. The light tan solid residue weighed 1.98 g. (theoretical weight assuming a quantitative conversion of hexamethylbenzene to pentamethylbenzyl chloride, 1.95 g.) and melted over the range 63–86° (lit.<sup>7</sup> m.p. for pentamethylbenzyl chloride, 82–84°).

Various tests, as outlined below, indicated that this crude product must have contained unreacted hexamethylbenzene and a polychloro derivative of the hydrocarbon as well as the monochloro compound. A sample of the product was recrystallized from hexane to provide white crystals of the impure monochloride which melted from 83 to 90°. Further recrystallization did not result in a narrowing of the melting range. The filtrate was evaporated to dryness and the residue recrystallized by dissolving it in acetone and chilling the solution. The white crystals thus obtained melted from 82 to 128°.

It was established by a sodium fusion analysis that the crude hexamethylbenzene halogenation product contained chlorine but no significant quantity of iodine. A weighed sample of this material was refluxed with alcoholic silver nitrate, and the precipitated silver chloride was collected, dried, and weighed. On this basis the Cl content of the halogenation product was found to be 18.3%; calcd. for  $C_6(CH_3)_5CH_2Cl$ , 18.1%.

Another sample, 0.693 g., of the crude hexamethylbenzene halogenation product in 25 ml. of ether was added dropwise to a slurry of 0.6 g. of lithium aluminum hydride in 30 ml. of ether.<sup>8</sup> The mixture was refluxed for 1 hr. after the addition was com-

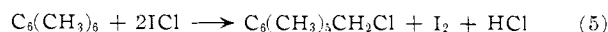
plete. The unreacted hydride was destroyed, and the mixture was acidified with dilute sulfuric acid. The ether phase was dried over sodium sulfate and concentrated to dryness to yield 0.548 g. of hexamethylbenzene, m.p. and mixture m.p. with an authentic sample 166–167°. The yield, based on the assumption that the material subjected to reduction was pure pentamethylbenzyl chloride, was 96%.

(b) **From Hexaethylbenzene and ICl.**—A 0.754-g. (0.00305 mole) sample of hexaethylbenzene was mixed with 1.00 g. (0.00615 mole) of iodine monochloride in carbon tetrachloride under much the same conditions as were used in investigating the products of the hexamethylbenzene reaction. The mixture was allowed to stand in the dark for 2 days at room temperature. It was established by a semiquantitative spectrophotometric analysis of the product solution that the conversion of ICl to  $I_2$  was then at least 90% complete. The crude product was isolated by the procedure described in section (a) above. The viscous semicrystalline oily material thus obtained weighed 0.740 g. (theoretical weight based on conversion of hexaethylbenzene to  $C_6(CH_2CH_3)_3CH(Cl)CH_3$ , 0.848 g.). Sodium fusion analysis of this material established that it contained chlorine but no significant quantity of iodine. A gravimetric analysis for chlorine based on refluxing of a sample of the crude product with silver nitrate indicated that it was 1.1% Cl; calcd. for  $C_6(CH_2CH_3)_3CH(Cl)CH_3$ , 12.6%. The crude product gave a positive test for unsaturation, as determined by treatment of its acetone solution with dilute aqueous potassium permanganate. The infrared spectrum of its carbon tetrachloride solution showed well defined bands at 895 and 1000  $cm^{-1}$  (lacking in the spectrum of hexaethylbenzene) which are characteristic of the out-of-plane CH vibration of a terminal vinyl group. A band characteristic of the C=C stretch (1600–1650  $cm^{-1}$ ) could not be detected with certainty because of solvent absorption in this region. No attempt was made to separate the various components of the product mixture.

**The Rate of Reaction of Pentamethylbenzyl Iodide with ICl.**—The procedure reported by Coleman and Hauser<sup>9</sup> for converting benzyl chloride to benzyl iodide was employed in preparing pentamethylbenzyl iodide from the corresponding chloride. The latter was prepared by the method of Aitken, Badger, and Cook.<sup>7</sup> A mixture of 2.6 g. of pentamethylbenzyl chloride and 0.3 g. of sodium iodide in 30 ml. of acetone was refluxed for 0.5 hr. The mixture was then poured into water and extracted with carbon tetrachloride. The extract was washed with aqueous sodium thiosulfate to remove iodine and, after drying with sodium sulfate, was then evaporated to dryness. The crude crystalline product weighed 3.2 g. A sample of this material was recrystallized once from hexane to provide a product of m.p. 101–103°; % I, 40.0; calcd. for  $C_{12}H_{17}I$ , 44.0. In the procedure used for the iodine analysis silver iodide was generated by refluxing a weighed sample of the organic halide with alcoholic silver nitrate. This material was used in making trial runs on the kinetics of reaction of pentamethylbenzyl iodide with iodine monochloride in carbon tetrachloride. Dilute solutions of the organic iodide and of ICl were mixed in absorption cells, and the production of iodine in these mixtures was followed by making optical density measurements at either 520 or 580  $m\mu$ . The reaction mixtures were initially about  $2 \times 10^{-3} M$  in ICl, and their initial organic iodide concentrations ranged from  $7 \times 10^{-4}$  to  $7 \times 10^{-3} M$ . In every case the liberation of iodine (1 mole per mole of the limiting reactant) appeared to be complete when mixing of the solutions was complete. Plans for making a more detailed study of the kinetics of this reaction were therefore abandoned.

## Results

**Stoichiometry of the Reactions.**—As has been discussed in detail in the Experimental section it has been established that in the hexamethylbenzene–ICl reaction in carbon tetrachloride 1 mole of iodine is produced for each 2 moles of iodine monochloride consumed, and 1 g.-atom of chlorine is simultaneously incorporated in the organic reactant. The over-all process can be described by



The crude organic product, which appears to be mainly

(9) G. H. Coleman and C. R. Hauser, *ibid.*, **50**, 1196 (1928).

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

(8) Cf. L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949), for application of this general procedure in the reduction of benzyl halides.

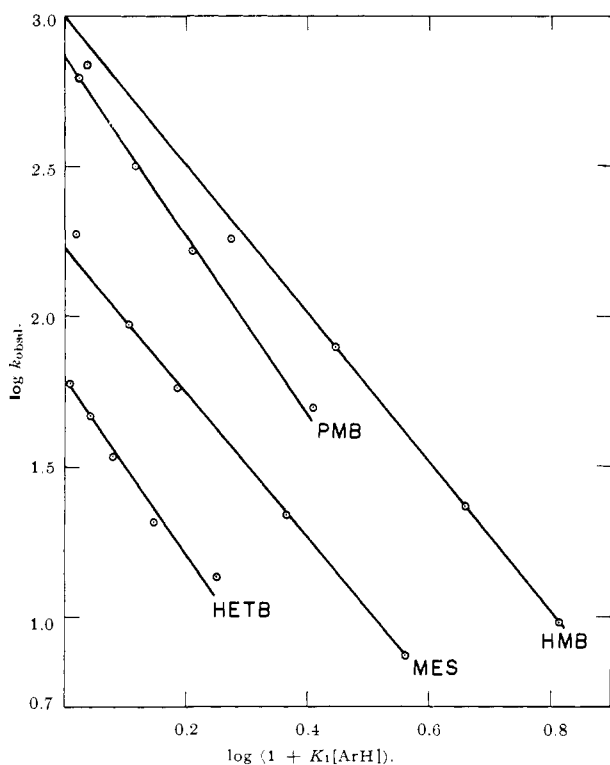


Fig. 1.—The dependence of  $k_{\text{obsd}}$  on the aromatic hydrocarbon concentration in the reaction of ICl with hexamethylbenzene (HMB), pentamethylbenzene (PMB), mesitylene (MES), and hexaethylbenzene (HETB). Initial values of  $[\text{ArH}]$  were used in plotting points for runs in which the hydrocarbon concentrations were very low.

pentamethylbenzyl chloride contaminated with some unreacted hexamethylbenzene and polychloro compounds, has been reduced essentially quantitatively to hexamethylbenzene by lithium aluminum hydride.

The product of the reaction of hexaethylbenzene and iodine monochloride in carbon tetrachloride also appears to be a mixture. It has a chlorine content which is considerably less than that of  $(\text{C}_2\text{H}_5)_5\text{C}_6\text{CH}(\text{Cl})\text{CH}_3$ . Very likely chlorohexaethylbenzene is formed initially in the reaction and to some extent loses hydrogen chloride, probably during the procedures used in isolating the product,<sup>10</sup> to form a substituted styrene.

**The Reaction Kinetics.**—In a typical rate run as conducted in this investigation the initial iodine monochloride concentration of the carbon tetrachloride solution was much less than that of the aromatic hydrocarbon (hexamethyl- or hexaethylbenzene). Plots of values of  $[\text{ICl}]_{\text{T}}^{-2}$  for such runs *vs.* the corresponding times have generally been found to be linear to relatively high percentages of completion. This is characteristic of a reaction which is third order with respect to the halogen. The term  $[\text{ICl}]_{\text{T}}$  is the sum (eq. 6) of the concentrations of free and complexed halogen.

$$[\text{ICl}]_{\text{T}} = [\text{ICl}] + [\text{C}_6\text{R}_6 \cdot \text{ICl}] \quad (6)$$

Rate constants  $k_{\text{obsd}}$  as defined in eq. 7 have been calculated from the slopes of these lines ( $k_{\text{obsd}} = \text{slope}/2[\text{C}_6\text{R}_6]$ ).

$$-d[\text{ICl}]_{\text{T}}/dt = k_{\text{obsd}}[\text{C}_6\text{R}_6][\text{ICl}]_{\text{T}}^3 \quad (7)$$

This is the same rate law which was used previously<sup>2</sup>

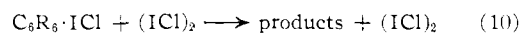
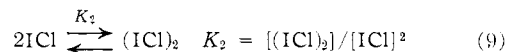
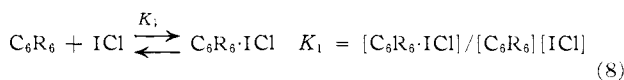
(10) For references concerning a similar instability of  $\alpha$ -phenylethyl chloride see E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 1194.

TABLE I  
RATE CONSTANTS FOR REACTION OF HEXAALKYLBENZENES  
WITH ICl ( $\text{CCl}_4$ , 24.7°)

Hexamethylbenzene			Hexaethylbenzene		
$10^3[\text{C}_6\text{R}_6]$ , mole/l.	$10^3[\text{ICl}]_{\text{T}}$ , mole/l.	$k_{\text{obsd}}$ , mole <sup>-2</sup> l. <sup>3</sup> sec. <sup>-1</sup>	$10^3[\text{C}_6\text{R}_6]$ , mole/l.	$10^3[\text{ICl}]_{\text{T}}$ , mole/l.	$k_{\text{obsd}}$ , mole <sup>-2</sup> l. <sup>3</sup> sec. <sup>-1</sup>
420	4.93	9.55	500	4.81	13.5
268	4.93	23.3	260	4.81	20.8
133	4.81	83.5	131	4.81	34.2
133	9.86	77.0	130	9.62	33.2
134	21.2	77.3	130	19.2	35.3
66.5	4.93	181	65.4	4.81	46.1
5.08	9.83	688	9.83	19.7	60.3

in interpreting successfully the results of the kinetic studies of the ring iodination of mesitylene and pentamethylbenzene by ICl in carbon tetrachloride. Runs have been made with both hexamethyl- and hexaethylbenzene in which the initial iodine monochloride concentration was twice the initial hydrocarbon concentration. For these runs  $k_{\text{obsd}}$  values have been calculated from the slopes of lines obtained by plotting  $[\text{ICl}]_{\text{T}}^{-3}$  *vs.* time ( $k_{\text{obsd}} = 2/3$  slope).

As indicated in the summary of runs in Table I, the values of  $k_{\text{obsd}}$  for a series of runs at fixed concentrations of the aromatic hydrocarbon are independent of a fourfold change in initial  $[\text{ICl}]_{\text{T}}$  values. On the other hand,  $k_{\text{obsd}}$  drops as the hydrocarbon content of the medium is increased. It is interesting to consider the reason for this drop, which is associated with formation of an aromatic hydrocarbon-ICl complex, in terms of a reaction path (eq. 8, 9, and 10) in which the complex is attacked by a dimer of ICl in the slow step (eq. 10);



it is assumed (see below) that a second molecule of ICl is consumed in a fast reaction following this slow step. Presumably the halogen dimer is present only in very small amounts in the reaction mixtures. It can be shown using eq. 8-10 that if this is the correct path,  $k_{\text{obsd}}$  is related to the aromatic hydrocarbon concentration as shown in eq. 11 in which  $n$  is the order of the over-all reaction with respect to ICl.

$$k_{\text{obsd}} = k_1 K_1 K_2 / (1 + K_1[\text{C}_6\text{R}_6])^n \quad (11)$$

As is required if this relationship is correct, it has been found that plots of  $\log k_{\text{obsd}}$  *vs.*  $\log(1 + K_1[\text{C}_6\text{R}_6])$  are linear for the reactions of both hexamethyl- and hexaethylbenzene. It has already been shown<sup>2,11</sup> that  $\log k_{\text{obsd}}$  values for iodination of mesitylene and pentamethylbenzene by ICl are linearly related to  $\log(1 + K_1[\text{ArH}])$ . Values of  $n$  and of  $k_1 K_1 K_2$ , which have been deduced from the slopes and intercepts of these plots (see Fig. 1), are summarized in Table II. The values of  $n$  for the reactions of the four aromatic hydrocarbons which are covered in this table range from 2.4-3.0, as compared to the value of 3 which has

(11) Unfortunately the equivalent of this relationship (eq. 11) which is used in ref. 2 is incorrectly stated in that reference. The relationships between  $k_{\text{obsd}}$  and the slopes of plots of  $[\text{ICl}]_{\text{T}}^{-2}$  or  $[\text{ICl}]_{\text{T}}^{-3}$  are also incorrectly stated in ref. 2. The  $k_{\text{obsd}}$  values which are reported in that paper are correctly defined by eq. 7 of this paper.

TABLE II  
VALUES OF  $n$ ,  $k_1K_1K_2$ , AND  $k_1K_2$  FOR REACTION OF  
POLYALKYLBENZENES WITH ICl (CCl<sub>4</sub>, 25°)

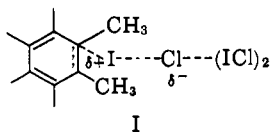
Polyalkylbenzene	$n$	$k_1K_1K_2$ , mole <sup>-3</sup> l. <sup>3</sup> sec. <sup>-1</sup>	$k_1K_2$ , <sup>a</sup> mole <sup>-2</sup> l. <sup>2</sup> sec. <sup>-1</sup>
Hexaethylbenzene	2.9	62	40
Mesitylene <sup>b</sup>	2.4	166	45
Pentamethylbenzene <sup>b</sup>	3.0	725	112
Hexamethylbenzene	2.5	1000	76

<sup>a</sup> The  $K_1$  values for formation of ICl complexes of the several hydrocarbons (CCl<sub>4</sub>, 25°) which were used in calculating  $k_1K_2$  were the most recent of the values reported by L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952), and N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **77**, 4202 (1955). <sup>b</sup> The values which are reported are based on data collected in the investigation described in ref. 2.

been deduced from analysis of rate data for individual runs. The constant  $k_1K_1K_2$  increases as the donor strength of the hydrocarbon (measured by  $K_1$ ) increases. The constant  $k_1K_2$ , which serves as a criterion of the relative reactivities of the several hydrocarbon-ICl complexes in the slow step of the reaction (eq. 10), is rather insensitive to changes in the identity of the hydrocarbon. Actually the hexamethylbenzene complex appears to be slightly less reactive than that of pentamethylbenzene; the difference in the observed  $k_1K_2$  values for these two compounds may, however, result to a considerable degree from experimental error.

It should be emphasized that the fact that there is a linear relationship between  $\log k_{\text{obsd}}$  and  $\log (1 + K_1 \cdot [C_6R_6])$  is not to be taken as evidence of the correctness of the proposed reaction path (eq. 8-10). Other paths, in which free hydrocarbon and free halogen molecules participate in the slow step, are in accord with this relationship. The reaction of eq. 10 is a likely choice for the slow step since, unlike alternate possibilities, it is bimolecular rather than polymolecular in character.

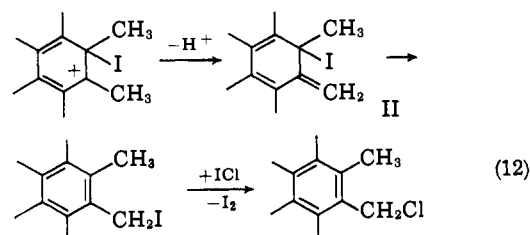
**The Reaction Mechanism.**—Because of the close similarities in the kinetic courses of the reactions of ICl in carbon tetrachloride which lead to ring iodination of mesitylene and pentamethylbenzene and to side-chain substitution of hexamethyl- and hexaethylbenzene it is concluded that in their rate-determining phases these processes are mechanistically alike. That is, it is assumed that the reactions of hexamethyl- and hexaethylbenzene proceed through electrophilic attack of ICl on the aromatic ring in the same way as is described in eq. 1 rather than by way of free-radical intermediates. The structure I is suggested for the transition state for the reaction of hexamethylbenzene.



Since  $k_1K_2$  values (Table II) are not highly sensitive to changes in the basicity of the reacting hydrocarbon, it might be concluded<sup>12</sup> that the transition state is

structurally more like a  $\pi$ - than a  $\sigma$ -complex and, therefore, not *highly* polar in character.

A variety of alternate follow processes which are similar in nature can be proposed in accounting for the conversion of the product of the slow step of the hexamethylbenzene reaction (which is considered to resemble I) to the final product. One possible reaction course is outlined



Transfer of halogen to the side-chain almost certainly takes place by way of an allylic rearrangement. The changes shown in the last two steps of this sequence might in fact take place in a cyclic process in which ICl attacks intermediate II to extract iodine from the ring and to attach chlorine at the side chain. It has previously been established that benzyl iodide reacts readily with ICl in carbon tetrachloride to form benzyl chloride.<sup>13</sup> This reaction occurs at an easily measurable rate in the dark at room temperature. There was no indication in the kinetic experiments on the hexamethylbenzene-ICl reaction that halogen consumption occurred in consecutive processes *with comparable rates*. It follows, therefore, that if the reaction actually proceeds as outlined in sequence 12, the last step in which pentamethylbenzyl iodide reacts with ICl must be extremely fast. As outlined in the Experimental section, it has been established by qualitative testing that this conversion does indeed take place so rapidly, even at very low initial reactant concentrations, that kinetic studies by conventional methods cannot be conducted.

It seems safe to assume that the reaction of hexaethylbenzene and ICl occurs by a stepwise process which is analogous to that for the side-chain halogenation of hexamethylbenzene. The iodine formed in small amounts during ring iodination of mesitylene and pentamethylbenzene is almost certainly the product of a competing reaction in which polymethylbenzyl chlorides are also formed. It has been observed<sup>2</sup> that the fraction of the iodine monochloride which appears as iodine in such reactions does not change with initial reactant concentrations. It follows that the simultaneous side-chain and ring halogenation processes must show the same rate dependence on reactant concentrations. They may well take place by way of a common intermediate.

**Acknowledgment.**—The authors are indebted to the National Science Foundation for a grant in support of this research.

- (12) F. R. Jensen and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4046 (1958).  
(13) R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 543 (1953).