The organic extracts yielded a yellow oil, bp 140–145° (0.1 mm), whose infrared spectrum indicated it to be a mixture of 3-phenylpropenyl and 3-phenylallyl mesityl ketones.

Preparation of α-Tetralone from 3-Phenylpropyl Mesityl Ketone.—A mixture of 5 g (0.02 mole) of 3-phenylpropyl mesityl ketone[15] and 3 g of aluminum chloride was heated under reflux in carbon disulfide for 12 hr. The mixture was then poured on ice and hydrochloric acid, and the organic material was extracted with ether, washed with water, dried, concentrated, and chromatographed on silica to remove the mesitylene. α-Tetralone was eluted with 1:1 petroleum ether–methylene chloride and identified by its infrared spectrum and preparation of its 2,4-dinitrophenylhydrazone derivative, mp 260° (lit.[23] mp 262°), yield 2.3 g (80%).

α-Tetralone was similarly obtained, along with mesitylene, in the reaction of mesityl cyclopropyl ketone with benzene in the presence of aluminum chloride.[15] Less tetralone was produced in this latter reaction if the mixture was stirred at room temperature overnight after mixing of the reagents and then heated under reflux for only 1 hr.

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(23) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

Iodine Formation in the Reaction of Polymethylbenzenes with Iodine Monochloride

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In acetic acid, hexamethylbenzene and pentamethylbenzene react with iodine monochloride by a process which is first order with respect to the aromatic hydrocarbon and second order in the halogen. In the reaction of hexamethylbenzene, iodine is produced and substitution of chlorine occurs at the aromatic side chain. The reaction of pentamethylbenzene appears to result mainly in ring iodination, although a small amount of free iodine is also formed. It is concluded that side-chain as well as ring substitution of the polymethylbenzenes is polar in nature and that, in the former reaction, a methylenecyclohexadiene serves as an intermediate. Some acetylated material, presumed to result from solvolysis of the initially formed haloaromatic substance, has been detected in the products of the hexamethylbenzene reaction. Side-chain chlorination of hexamethylbenzene by iodine monochloride also occurs in nitromethane solution. Unlike the corresponding reaction in acetic acid, halogenation in this solvent is self-inhibiting. Apparently, hydrogen chloride generated in the reaction forms a complex with iodine monochloride which is much less reactive than the free halogen.

It has been established previously[1] that hexamethylbenzene reacts with iodine monochloride in carbon tetrachloride to form pentamethylbenzyl chloride (eq 1). The reaction of pentamethylbenzene and

$$C_6(CH_3)_6 + 2ICl \longrightarrow C_6(CH_3)_5CH_2Cl + I_2 + HCl \quad (1)$$

iodine monochloride in carbon tetrachloride results mainly in the formation of pentamethyliodobenzene $C_6(CH_3)_5I$, a fact which suggests that halogenation occurs by a polar rather than a homolytic process. Since the rate laws for the halogenation of the two polymethylbenzenes are both of the form[1,2]

$$-d[ICl]/dt = k[ArH][ICl]^2 \quad (2)$$

it has been concluded that side-chain chlorination of hexamethylbenzene by iodine monochloride also occurs by a polar process which is mechanistically similar in character to the pentamethylbenzene reaction. The ring iodination of pentamethylbenzene by ICl is accompanied by the formation of some molecular iodine.

The investigation of iodine monochloride as a halogenating agent for penta- and hexamethylbenzene has now been extended mainly to determine the influence on the course of the reactions of shifting from carbon tetrachloride to more polar solvents. This brief report is concerned largely with the reactions in acetic acid and in nitromethane. Confirming evidence is also presented that, as has previously been assumed, the iodine formed in the pentamethylbenzene reaction in carbon tetrachloride is produced (eq 3) simultaneously with side-chain-chlorinated pentamethylbenzene (see Experimental Section).

$$C_6H(CH_3)_5 + 2ICl \longrightarrow C_6H(CH_3)_4CH_2Cl + I_2 + HCl \quad (3)$$

Experimental Section

Kinetics of Reaction of the Polymethylbenzenes and ICl.—Acetic acid[3] and nitromethane[4] were purified for solvent use as described previously. Iodine monochloride was prepared from the elemental halogens.[5] Eastman Organic Chemicals penta- and hexamethylbenzenes were used without further purification. The methods employed in preparing rate samples and in following the course of the reactions by spectrophotometric methods (using 1-cm absorption cells as reaction vessels) were closely similar to those applied in earlier rate work on the polyalkylbenzene–ICl reaction with carbon tetrachloride as the solvent.[1,2] Stock solutions of iodine monochloride and iodine (the latter prepared from the reagent grade halogen) were standardized by iodometric methods.

In the runs with pentamethylbenzene as the reacting hydrocarbon, the quantities of iodine monochloride consumed and of iodine formed were calculated (eq 4 and 5) from optical densities, *d*, of the solutions which were measured from time to time at two different wavelengths (λ_1 and λ_2). For reactions in acetic acid, wavelengths of 500 mμ and either 370, 420, or 430 mμ were used. For reactions in nitromethane, the two wavelengths were 500 and 420 mμ. The extinction coefficients, ϵ and ϵ' were determined separately for each reaction mixture since they vary with changes in the aromatic hydrocarbon concentration of the medium. The reactions were generally followed to high percentages (75% or more) of completion.

$$d_{\lambda_1} = \epsilon_{ICl}[ICl] + \epsilon_{I_2}[I_2] \quad (4)$$

$$d_{\lambda_2} = \epsilon'_{ICl}[ICl] + \epsilon'_{I_2}[I_2] \quad (5)$$

In investigating the reactions of hexamethylbenzene, a single wavelength, either 550 or 580 mμ, was employed in individual rate runs. The ICl concentrations during the course of the runs were calculated[1] from these readings and initial ICl concentrations on the assumption that 2 moles of the reacting halogen were consumed in forming 1 mole of iodine.

In the runs with both penta- and hexamethylbenzene, hydrogen chloride was produced in appreciable quantity. It was established by separate experiment that in acetic acid the extinction

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

(2) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412 (1957).

(3) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).

(4) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 1063 (1959).

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

coefficients of both iodine (2×10^{-3} M) and iodine monochloride (0.01 M) in the wavelength region of the rate measurements were not altered significantly by introduction of the hydrogen halide at a concentration level as high as 0.01 M. In nitromethane, however, the extinction coefficients both of iodine and iodine monochloride are affected by hydrogen chloride and very seriously so, at the lower of the two wavelengths used in studying the pentamethylbenzene reaction. At 420 mμ, for example, the optical densities of 0.0138 M iodine monochloride and 0.00162 M iodine solutions in acetic acid are changed from 1.40 to 0.740 and from 0.259 to 0.940, respectively, by the introduction of HCl at 0.01 M concentration. The change in the ICl absorption is very likely the result of $HICl_2$ formation. This assumption is supported by the observation that the rates of the penta- and hexamethylbenzene reactions in nitromethane fall off very markedly even in their early phases, very likely because the unreacted iodine monochloride is deactivated by complexing with the hydrogen chloride. Because of the combined complications of rate retardation by hydrogen chloride and the effects of the hydrogen halide on the spectrum of the halogens in nitromethane, a satisfactory analysis of the kinetics of the pentamethylbenzene reaction has not been achieved. The hexamethylbenzene reactions have been investigated at wavelengths at which iodine concentration can be estimated with reasonable accuracy even in the presence of an appreciable quantity of hydrogen chloride.

Previously, some evidence has been obtained of rate inhibition by HCl produced in the ring iodination of mesitylene by ICl in acetic acid, and this has been ascribed to $HICl_2$ formation.[6] Such inhibition has not been observed in the current studies of the reactions of more highly methylated benzenes in acetic acid.

Side-Chain Chlorination of Pentamethylbenzene in Its Reaction with Iodine Monochloride in Carbon Tetrachloride.—A carbon tetrachloride solution initially containing 2.88 g (0.0194 mole) of pentamethylbenzene and 3.15 g (0.0194 mole) of iodine monochloride (100 ml total volume) was stored in the dark for 6 days after preparation. The iodine and hydrogen chloride in the solution of the reaction products was removed by washing successively with sodium thiosulfate and sodium hydroxide solutions, and the carbon tetrachloride was removed under vacuum.

A portion of the solid product was analyzed qualitatively for side-chain halogen through refluxing of a sample with an aqueous ethanol solution of sodium hydroxide. The cooled mixture was diluted with water, acidified with nitric acid, and filtered to remove organic solids. A sample of the filtrate gave a positive test for halide on treatment with silver nitrate solution. It was concluded that the halide precipitated by silver ion was chloride rather than iodide since a second sample of the filtrate gave no iodine coloration on gassing with chlorine.

A second sample of the solid reaction product was analyzed quantitatively for side-chain-substituted chlorine by reflux with an aqueous ethanol solution of silver nitrate followed by collection and weighing of the precipitated silver chloride. On this basis the product mixture was estimated to be 1.03 wt% Cl.

The results of rate runs conducted in the previous work[2] on the pentamethylbenzene–ICl reaction in carbon tetrachloride have been reexamined to determine the fraction of ICl which is converted to iodine. The pertinent results are incorporated in Table I. On the average, at 25° 16.8% of the reacting iodine monochloride is converted to iodine. On the assumption that side-chain chlorination products of pentamethylbenzene and iodine should form in equimolar quantity, it has been calculated that the organic matter isolated from the solution of the products of reaction of pentamethylbenzene and ICl, as described above, should contain 1.15 wt % Cl.

The Products of Reaction of Hexamethylbenzene and ICl. A. In Acetic Acid.—A solution initially containing 0.472 g (0.00291 mole) of hexamethylbenzene and 0.944 g (0.00580 mole) of iodine monochloride in a total volume of 100 ml in acetic acid was stored in the dark for 16 days. By spectrophotometric methods, it was estimated that the resultant solution contained iodine in 91% of the quantity theoretical for its formation according to eq 1. The solution was freed of iodine by the addition of 300 ml of dilute aqueous sodium thiosulfate, and the resultant mixture was extracted several times with carbon tetrachloride. The combined extracts were washed with dilute sodium hydroxide solution, dried over sodium sulfate, and evaporated to dryness to provide the crude product (a greenish yellow powder, mp 108–138°). Treatment of a hot ethanol solution of a sample of this material with aqueous alcoholic silver nitrate resulted in the formation of a substantial silver halide precipitate. That the halide was chloride rather than iodide was established through sodium fusion of a separate sample. Gravimetric analysis for solvolyzable chloride, by precipitation of silver chloride as described above, indicated that the material was 6.63% Cl (calcd for $C_{12}H_{17}Cl$, 18.1%). The infrared spectrum of the crude product of the halogenation reaction (carbon tetrachloride solution) showed moderately strong peaks at 1750 (ester C═O stretch) and 1260 cm^{-1} (asymmetric C—O—C stretch). Undoubtedly, some ester was present in the product mixture; presumably it was formed by acetolysis of side-chain-chlorinated material ($ArCH_2Cl + HOAc \rightarrow ArCH_2OAc$). Evidence has been presented previously of the formation of acetates in the reaction of chlorine[7] and bromine[8] with hexamethylbenzene in acetic acid.

TABLE I

IODINE FORMATION IN THE REACTION OF PENTAMETHYLBENZENE AND IODINE MONOCHLORIDE IN CARBON TETRACHLORIDE[a]

$[C_6H(CH_3)_5]_i$, M	$[ICl]_i$, M	Moles of ICl consumed converted to I_2,[b] %	Moles of ICl consumed,[c] %
	At 25.2°		
0.244	0.0053	17.2	83
0.0974	0.0053	15.8	81
0.0487	0.00267	17.4	62
0.0966	0.0072	14.5	86
0.0966	0.0036	16.1	72
0.0966	0.00179	19.1	49
0.00864	0.00870	17.5	61
	At 45.7°		
0.00835	0.00841	27.6	57

[a] Supplementary information relating to rate runs made in connection with an earlier investigation.[2] [b] The indicated percentages correspond to $2[I_2]_t/([ICl]_i - [ICl]_t) \times 100$. These percentages were observed to remain constant during the course of the runs. [c] Extent of completion of reaction at the time the measurement was made.

B. In Nitromethane.—A solution initially containing 1.044 g (0.00644 mole) of hexamethylbenzene and 2.091 g (0.01288 mole) of iodine monochloride in nitromethane was stored in the dark for 4 days. It was established by spectrophotometric measurement that at this time over 80% of the iodine monochloride was converted to iodine. The solid organic products were recovered from the solvent in much the same fashion as described for the products of reaction in acetic acid. This material, a waxy yellow powder of mp 86–140°, contained chlorine but no iodine, as established by sodium fusion. It was established (by refluxing a weighed sample with alcoholic silver nitrate and collecting the precipitated silver chloride) that this material contained 7.45 wt% Cl (calcd for $C_{12}H_{17}Cl$, 18.1%). Very likely side-chain chlorine was lost through hydrolysis during product work-up.[7b]

Results

As is the case when carbon tetrachloride is the solvent, iodine monochloride reacts with hexamethylbenzene in acetic acid to produce 1 mole of iodine for each 2 moles of the mixed halogen which are consumed. The organic substance which is produced appears to be a mixture of side-chain-chlorinated hexamethylbenzene and its acetolysis product. The reaction of pentamethylbenzene and iodine monochloride in acetic acid leads to the production of some iodine (see Table II), though (at 25 and 45°) less than that formed in the corresponding reaction in carbon tetrachloride.

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(6) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 5623 (1956).

(7) (a) E. Baciocchi and G. Illuminati, *Gazz. Chim. Ital.*, **92**, 89 (1962); (b) E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Am. Chem. Soc.*, **87**, 3953 (1965).

(8) R. Josephson, R. M. Keefer, and L. J. Andrews, *ibid.*, **83**, 3562 (1961).

TABLE II

RATE CONSTANTS (EQ 6) FOR REACTION OF POLYALKYLBENZENES (ArH) AND ICl IN ACETIC ACID[a]

$[ArH]_i$, M	$[ICl]_i$, M	k_{obsd}, mole^{-2} sec^{-1} l^2
ArH = Pentamethylbenzene (25.0°)		
0.398	0.01515	0.104[b]
0.398	0.00379	0.107
0.398	0.00363	0.123
0.201	0.01424	0.120
0.199	0.01515	0.114[c]
0.199	0.00363	0.133[d]
0.100	0.01424	0.116
0.100	0.00712	0.104[e]
ArH = Hexamethylbenzene (25.0°)		
0.0511	0.01733	0.019
0.0511	0.00866	0.020
0.0511	0.00484	0.017
0.0256	0.01733	0.027
ArH = Hexamethylbenzene (44.8°)		
0.0491	0.0171	0.159
0.0491	0.00855	0.159
ArH = Pentamethylbenzene (44.8°)		
0.200	0.01532	0.446[f]
0.200	0.00766	0.469[g]

[a] Pentamethylbenzene runs were carried to 75% or more of completion in most cases; those with hexamethylbenzene were carried to better than 50% of completion. [b-e] Percentage of reacted ICl which was converted to iodine = 6.6, 4.6, 6.6, and 5.1, respectively. These percentages, which apply to completion of reaction, are similar to those observed at intermediate stages of the reaction. [f,g] Percentage of total ICl converted to iodine = 5.8, 6.4, respectively. These percentages, which apply to completion of reaction, are similar to those observed at intermediate stages of the reaction.

Lambourne and Robertson,[9] who previously detected iodine in the products of pentamethylbenzene halogenation by iodine monochloride in acetic acid, have assumed that it was formed simultaneously with ring-chlorinated material [$ClC_6(CH_3)_5$]. As noted above, the results of the current investigation of the reaction in carbon tetrachloride indicate, however, that iodine formation is an adjunct of side-chain rather than ring chlorination.

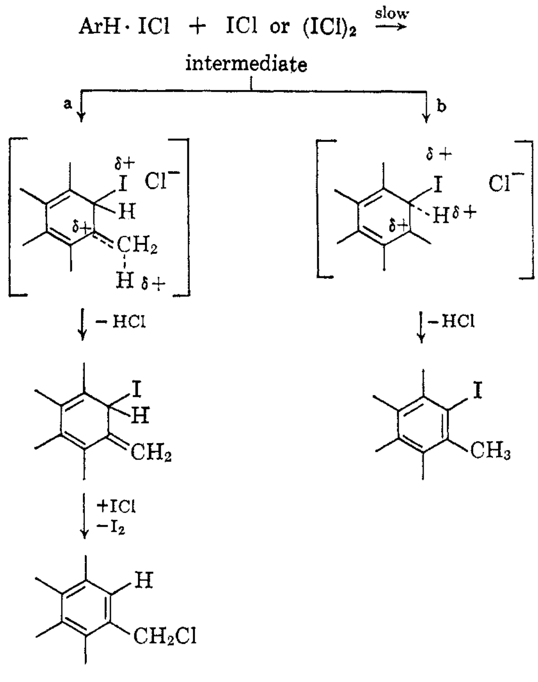
The reactions of both penta- and hexamethylbenzene in acetic acid conform to the rate law (eq 6) which previously has been found to apply to the ring iodination of mesitylene by ICl in acetic acid.[6] The various

$$-d[ICl]/dt = k_{obsd}[ArH][ICl]^2 \qquad (6)$$

runs which were made to establish this rate law are summarized in Table II. The rate constants listed are calculated from the slopes of plots of 1/[ICl] *vs.* time, which in every case were linear to at least 50% completion of the reaction. Although there is some evidence that iodinations of alkylbenzenes by iodine monochloride in acetic acid are subject to inhibition by hydrogen chloride,[6] it is only in the later phases of the reactions (as conducted in this investigation) that the rates are seriously affected.

Because the form of the rate law is the same for the reactions of mesitylene and penta- and hexamethylbenzene in acetic acid, it is concluded that these reactions have rate-determining steps which are closely similar. Very possibly, the reactions leading to ring and side-chain halogenation of pentamethylbenzene share a common intermediate. In accounting for the fact that the reactions of ICl and alkylbenzenes are fourth and third order, respectively, in acetic acid and in carbon tetrachloride, it has been suggested previously[2] that a 1:1 aromatic–ICl complex is subject to attack by ICl or its dimer in the slow step leading to production of the intermediate in question.

The fact that more side-chain halogenation of pentamethylbenzene occurs in the reaction in carbon tetrachloride than in acetic acid deserves brief attention. For purposes of discussion, a reactive intermediate formed in the slow step of the reaction can be assumed to collapse to products by either of two alternate paths (7a,b). The bracketed structures are introduced to approximate the distribution of positive charge in the transition states. Since this charge is more dispersed in path a than in b, it is reasoned, in accord with experimental observation, that the fraction of reaction proceeding by path a should increase with a shift from a polar to a nonpolar solvent. Underlying this reasoning is the assumption that the rate changes for these two paths which accompany the change in solvent are controlled primarily by changes in activation energy.[10,11] That this assumption is not fully justified and can be used as the basis for a contradictory prediction is suggested by the fact that in acetic acid the fraction of reaction which leads to iodine production is essentially temperature independent (see footnotes, Table II), while in carbon tetrachloride this fraction increases with temperature. This would seem to indicate that in acetic acid the activation energies for paths a and b are the same, and that the change to carbon tetrachloride should diminish the



(7)

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[9] L. J. Lambourne and P. W. Robertson, *J. Chem. Soc.*, 1167 (1947).

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 347.

(11) As noted by a referee, in both of the bracketed structures positive charge is also subject to dispersal through delocalization of the π electrons of the rings. The above argument cannot, therefore, be used to predict great sensitivity of reaction path to changes in solvent, and in fact the change of solvent from carbon tetrachloride to acetic acid does not have a drastic effect on the course of the pentamethylbenzene–ICl reaction. The referee also observes and the authors concur, that acetoxy derivatives which form during the course of the reactions under consideration may form through reaction of solvent with the iodomethylenecyclohexadiene intermediate (path a, reaction 7) rather than with pentamethylbenzyl chloride. The reactions summarized in path a bring to mind the study of 1,1,2,3,4,5,6-heptamethylbenzenonium ion, which in aqueous acid solutions has been shown to be in equilibrium with a neutral molecule, presumably 4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5: *cf.* W. v. E. Doering, M. Saunders, H. G. Boynton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

importance of path a. It is interesting that k_{obsd} values (eq 6) for the reactions of mesitylene,[6] pentamethylbenzene, and hexamethylbenzene in acetic acid are in the approximate ratio 1:1:0.2. Because of favorable electronic effects of polyalkylation of the aromatic nucleus, pentamethylbenzene is usually substantially more reactive than mesitylene in electrophilic substitution processes. The relatively low reactivity of pentamethylbenzene, as well as that of hexamethylbenzene with ICl, is ascribed to a screening of the π electrons of the ring from attack by the bulky halogen when the ring is highly substituted.[12] The enormity of the steric effect is indicated by the differences in the energies of activation for the reactions of penta- ($E_a = 12.5 \pm 0.6$ kcal/mole) and hexamethylbenzene ($E_a = 20.2$ kcal/mole); the corresponding entropies of activation are -20.1 ± 2 and -0.7 eu, respectively. These values have been calculated, respectively, from rate constants for runs at 25.0 and 44.8° (Table II) in which initial concentrations of penta- and hexamethylbenzene were, respectively, 0.2 and 0.05 M. It should be noted that the k_{obsd} value for the hexamethylbenzene reaction appears to increase somewhat with decreasing aromatic reactant concentration, and this is attributed to complex formation between the reactants.

In its early phases the iodine-producing reaction of hexamethylbenzene with ICl in nitromethane conforms to the same rate law (eq 6) which applies to the reaction (eq 1) in acetic acid. An explanation of the deviations from this rate law in later phases of reaction is given in the Experimental Section. The k_{obsd} values based on initial slopes of plots of $1/[\mathrm{ICl}]$ *vs.* time for several runs with nitromethane as solvent are listed in Table III. At the outset, at least, hexamethylbenzene is considerably more reactive in nitromethane than in acetic acid (*cf.* Table II). It has been observed previously that aromatic chlorination occurs more rapidly in nitromethane than in acetic acid.[4]

TABLE III

INITIAL RATE CONSTANTS FOR THE REACTION OF HEXAMETHYLBENZENE AND ICl IN NITROMETHANE (25.0°)

$[\mathrm{ArH}]_i$, M	$[\mathrm{ICl}]_i$, M	k_{obsd}, mole^{-2} sec^{-1} l^2	Extent of reaction,[a] %
0.0340	0.01295	4.24[b]	20
0.0340	0.00647	4.35[b]	15
0.0342	0.00647	3.94[c]	12
0.0171	0.00323	3.75[c]	9

[a] The per cent of ICl consumed before deviations from the assumed rate law (eq 6) were observed. [b,c] The reactions were followed by spectrophotometric analysis for iodine at wavelengths of 580 and 550 mμ, respectively. These reactions slowed almost to a halt when 70–80% of the ICl was consumed.

Because of difficulties in establishing ICl concentrations in the presence of HCl in nitromethane by spectrophotometric methods, a satisfactory quantitative interpretation of the results of kinetic studies for the ICl–pentamethylbenzene reaction in this solvent has not been achieved (see Experimental Section for details). By analysis of final products of mixtures initially 0.1 M in pentamethylbenzene and 0.01 M (or less) in ICl in nitromethane, it has been established that at 25° about 6% of the reacting halogen is converted to iodine. As is the case for reaction in acetic acid, this figure is substantially less than that for reaction in carbon tetrachloride.

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

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(12) A reversal in the normal reactivities of mesitylene and pentamethylbenzene in their zinc chloride catalyzed reactions with ICl in acetic acid has been similarly explained.[6]

Conformational Analysis. V.[1,2] 2-Chloro- and 2-Bromotetrahydropyran

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The sole detectable conformation of both 2-chloro- and 2-bromotetrahydropyran has been found to be that containing the halogen in the axial position. Solvent polarity has no measurable effect on decreasing the fraction of the axial conformer. An estimate of the magnitude of the "anomeric effect" is made and compared with that of the α-halo ketone effect.

The determination of the conformational equilibrium of mobile systems by nmr spectroscopy has been extremely fruitful.[3] The experimental approaches depend on conformationally homogeneous models from which either the chemical shifts or nuclear spin couplings can be obtained. If model substrates are not available, semiquantitative methods can still be applied. By examining a mobile system at reduced temperatures, the conformational isomers may be frozen out, and an estimate of the equilibrium constant can be obtained if the chemical shifts of the reference proton in the two conformers are sufficiently different. However, the percentage of the unstable conformer may be so low at reduced temperatures that the equilibrium constant cannot be determined accurately by this method.[4] At ambient temperatures the equilibrium constant will normally tend to reflect an increase in the percentage of the unstable conformer, and conformational analysis of a mobile system can then be ap-

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(1) Paper IV: R. J. Ouellette, G. E. Booth, and K. Liptak, *J. Am. Chem. Soc.*, **87**, 3436 (1965).

(2) The authors acknowledge a grant-in-aid from The Ohio State University in partial support of this research. A Petroleum Research Fund Grant is also acknowledged. We wish to thank the NSF for grants used for the purchase of the nmr spectrometer.

(3) (a) E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, 97 (1962); (b) A. H. Lewin and S. Winstein, *J. Am. Chem. Soc.*, **84**, 2464 (1962); (c) W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963); (d) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 747 (1962); (e) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962).

(4) H. Feltkamp and N. C. Franklin, *ibid.*, **87**, 1616 (1965).