

Long-Range Effects in the Alkylation of Benzene with Polyhalooctanes

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The pseudo-first-order rate constants for the hydrogen fluoride-boron trifluoride catalyzed reaction of benzene with three different series of polyhalooctanes were measured. Each series of polyhalooctanes is comprised of isomers which differ only in the position of attachment of the reactive secondary chloro group relative to the unreactive primary substituents. The 1-bromo, 1,1-dichloro, and 1,1,1-trichloro groups are shown to decrease the rate of reaction of a secondary chloro group, relative to the unsubstituted case, even when separated by seven methylene units. The influence of these primary substituents is shown to decrease by a constant attenuation factor of 0.59 per methylene unit.

We previously described our investigation of the alkylation of benzene with a series of dichlorooctane isomers which contained both primary and secondary chloro groups.¹ The hydrogen fluoride-boron trifluoride catalyst system permitted reaction of the secondary chloro group, leaving the primary chloro group unchanged. We now wish to report our results of alkylations with three other series of polyhaloalkane isomers. These are the 1-bromo-X-chlorooctane, 1,1,X-trichlorooctane, and 1,1,1,X-tetrachlorooctane series.² In each series the substituents at C-1 were shown to be unreactive under the conditions used.

1-Bromo-X-Chlorooctanes.—This series of isomers was prepared by radical chlorination of 1-bromooctane to about 20% conversion. The dihalooctane fraction was shown by vapor phase chromatography (vpc) to be comprised of eight isomers. These were assumed to be the 1-bromo-1-chloro-, 1-bromo-2-chloro-, through 1-bromo-8-chlorooctane isomers in "numerical order"³ of elution. A rigorous identification of the isomers was not attempted, although there are excellent grounds for the above assignments. Thus, chlorination of 1-chlorooctane yielded eight isomers which eluted from the same vpc column in "numerical order";¹ by analogy, 1-bromo-X-chlorooctane would be expected to behave in the same manner. In the 1,X-dichlorooctane series, each isomer was found to be present in greater quantity than the preceding isomer in the "numerical order" of elution;⁴ the same pattern was found for 1-bromo-X-chlorooctane. The 1-bromo-3-chloro- and 1-bromo-8-chlorooctane isomers were isolated and identified as the third and eighth peaks, respectively.

The alkylation procedure was identical with that used in previously described work with 1,X-dichlorooctane.¹ Boron trifluoride was passed slowly into a stirred solution of the mixed dihalooctanes in excess benzene and liquid hydrogen fluoride at 0°.

The reaction was followed by vpc as a function of time. The 1-bromo-1-chloro-, 1-bromo-2-chloro-, and 1-bromo-8-chlorooctane isomers were unchanged after 6 hr, as shown by vpc analysis using an internal standard. The reaction was found to be pseudo first order in each of the alkylating agents. The results of the kinetic treatment are shown in Table I.

The products were identified as the 7-, 6-, 5-, and 4-phenyl-1-bromooctanes, and were formed in the

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR
THE REACTIONS OF BENZENE WITH POLYHALOOCTANES
USING HF/BF₃ AS CATALYST AT 0°

Compd	$k \times 10^4, \text{sec}^{-1}$				
	X = 3	X = 4	X = 5	X = 6	X = 7
X-Chlorooctane	58	58	58	58	58
1,X-Dichlorooctane	0.71	8.0	17	26	35
1,1,X-Trichlorooctane	...	2.1	7.5	18	28
1,1,1,X-Tetrachlorooctane	...	0.8	4.8	14	25
1-Bromo-X-chlorooctane	1.0	9.7	21	33	42

TABLE II
WEIGHT PER CENT PRODUCTS FROM REACTIONS
OF BENZENE WITH POLYHALOOCTANES
USING HF/BF₃ AT 0°

1-substituent	Phenyl position			
	7	6	5	4
Cl	53	29	14	4
Cl ₂	62	29	8	1
Cl ₃	58	34	6	2
Br	50	31	15	4

proportions shown in Table II. These products were identical and in the same proportion in each sample regardless of the time of sampling.

1,1,X-Trichlorooctanes.—Treatment of octanal with phosphorus pentachloride yielded 1,1-dichlorooctane, which, upon free-radical-catalyzed chlorination, gave the 1,1,X-trichlorooctane series of isomers. By analogy with the 1,X-dichlorooctane series, it was assumed that these isomers eluted in "numerical order."⁵ Furthermore, the 1,1,1 isomer was synthesized; and the 1,1,2, 1,1,3, and 1,1,8 isomers were trapped from a vpc column and identified spectroscopically.

The alkylation procedure was identical with that previously described. The 1,1,1, 1,1,2, 1,1,3, and 1,1,8 isomers were unchanged. The pseudo-first-order rate constants for the reaction of the remaining isomers are shown in Table I.

The products did not vary as a function of time, nor did their relative proportions. The products were 7-, 6-, 5-, and 4-phenyl-1,1-dichlorooctanes in the relative amounts shown in Table II.

1,1,1,X-Tetrachlorooctanes.—The radical-catalyzed addition of chloroform to 1-heptene gave 1,1,1-trichlorooctane,⁶ which, upon radical chlorination, gave the 1,1,1,X-tetrachlorooctane isomer series. Seven

(1) D. L. Ransley, *J. Org. Chem.*, **33**, 1517 (1968).

(2) X represents the position of chloro group attachment to each available carbon atom in turn; e.g. 1,1,X-trichlorooctane represents the 1,1,1-, 1,1,2-, 1,1,3-, 1,1,4-, 1,1,5-, 1,1,6-, 1,1,7-, and 1,1,8-trichlorooctane mixture.

(3) "Numerical order" is the order shown in the example in ref 2.

(4) With the exception of the isomer with longest retention time, i.e., when X = 8.

(5) The 1,1,3 isomer eluted before the 1,1,2 isomer in this series. However, the 1,1,3 isomer was present in greater quantities than the 1,1,2 isomer; hence, the relative amounts of the isomers is probably a better indication that the remaining isomers eluted in "numerical order."

(6) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1100 (1947).

peaks were evident in the chromatogram of this isomer mixture. There were increasing proportions of the isomers with increasing retention time,⁴ and once more it was assumed that elution was in "numerical order." Supporting evidence for this assumption was provided by synthesis of the 1,1,1,3 isomer and recognition of distinctive spectroscopic features of the 1,1,1,6, 1,1,1,7, and 1,1,1,8 isomers in fractions concentrated by vpc.

The kinetic data for the alkylation reactions run under the previously described conditions are shown in Table I. The proportions of the products, 7-, 6-, 5-, and 4-phenyl-1,1,1-trichlorooctanes, were the same in each sample and are shown in Table II.

Discussion

The use of liquid hydrogen fluoride and boron trifluoride as a catalyst system for the alkylation of benzene provides a unique opportunity to study the influence of several unreactive groups on the reaction at the site of the secondary chloro group. The alkylation reactions under consideration involve ionization of a secondary chloro group to produce a carbonium ion. Any electron-withdrawing influence of the unreactive groups at the reaction site would increase the energy requirements of this process and thereby decrease the rate of reaction.

We have demonstrated that the 1-bromo, 1,1-dichloro, and 1,1,1-trichloro groups do not react under the conditions used. By running competition rate experiments within each isomeric series, the change of the influence of the unreactive group with distance from the reaction site may be observed. By running each series of reactions under identical conditions, the relative influence of the unreactive groups may be compared.

The reactions were shown to be pseudo first order in each alkylating agent. The observed first-order rate constants are shown in Table I and are compared with the data for the similar reactions of 1,X-dichlorooctane and secondary monochlorooctane obtained in previous work.¹

In qualitative terms we see that the reaction rate increases as the distance between the secondary chloro group and the unreactive, electron-withdrawing group increases. However, in each series the 7-chloro isomer reacts more slowly than the unsubstituted monochlorooctanes. This indicates that the influence of the substituents at C-1 is still appreciable at C-7.

Peterson and coworkers have recently demonstrated that the influence of remote substituents, varying by a constant factor per methylene unit, on the addition of trifluoroacetic acid to olefins, can extend over 11 methylene units.⁷ From a familiar⁸ empirical treatment, $\log(\log k_H - \log k_X)$ ⁹ was successfully plotted as a linear function vs. the number of methylene units separating the substituent and the site at which the charge was generated.

Figure 1 shows the result of treating the data of Table I in this manner. Remarkably good linear plots are obtained for the four cases under consideration.

(7) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Amer. Chem. Soc.*, **87**, 5183 (1965).

(8) See ref 1 and 7 and references therein.

(9) k_H = rate constant for the unsubstituted reaction; k_X = rate constant for the substituted case.

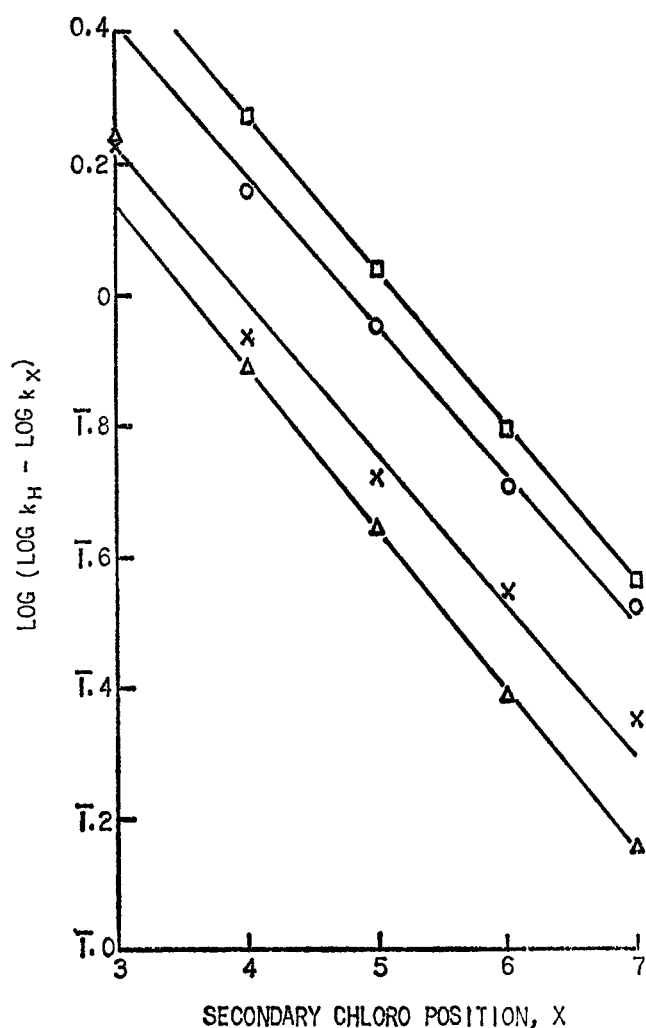


Figure 1.—Plot of rate data for alkylations with polyhalooctanes, assuming the substituent effect falls off by a constant factor per methylene unit: X, 1,X-dichlorooctanes; O, 1,1,X-trichlorooctanes; □, 1,1,1,X-tetrachlorooctanes; Δ, 1-bromo-X-chlorooctanes.

The slope of the lines is the log of the attenuation factor.⁷ The average value for the attenuation factor from our four systems is 0.59. This compares with 0.65 obtained by Peterson⁷ and 0.53 by Stevenson and Williamson¹⁰ in correlating pK values for a series of ω-cyanoamines.

The relative proportions of the reaction products are shown in Table II. There is a greater tendency for phenyl attachment at positions remote from the unreactive, electron-withdrawing group. Within each series, ionization of the secondary chloro group is the slow step. The carbonium ion rapidly isomerizes, presumably by a series of 1,2 hydride shifts. Thus, within each series, there is a common intermediate. The product proportions are dependent on the substituents at C-1. The tendency is for the groups with the strongest electron-withdrawing influence to favor phenyl attachment at the most remote secondary carbon atoms. Alkylation on benzene is a rapid and irreversible¹ process under the conditions used.

We had planned to include the reaction of 1-fluoro-X-chlorooctane with benzene in our study. However, the 1-fluoro group appears to react somewhat faster

(10) G. W. Stevenson and D. Williamson, *J. Amer. Chem. Soc.*, **80**, 5943 (1958).

than secondary chloro compounds. The reaction products, 1-fluorophenyl-, chlorophenyl-, and diphenyloctanes, were not investigated in detail.

At this point we should add a note concerning the catalyst system. To the best of our knowledge the combination of hydrogen fluoride and boron trifluoride as a catalyst system for the alkylation of aromatic compounds with alkyl halides has not been used previously.¹¹ The rapid rates at ambient temperatures, excellent yields, and high degree of selectivity between primary and secondary substituents make this a most interesting system. However, there are some unusual features of this system.

Reaction did not start as soon as boron trifluoride was passed into the system, but did so quite abruptly after boron trifluoride has passed for about 20 min in our work with 0.1 mol of alkylating agent.¹² In our competition reactions, each isomer started to react at about the same time.

Experimental Section

1-Bromo-X-Chlorooctane.—Into a 1-l. turbomixer, with an internal cooling coil and gas inlet at the bottom, was placed 499 g (2.58 mol) of 1-bromooctane. Nitrogen was bubbled through the mixture for 30 min. Chlorine was then passed with rapid stirring at about 25° for 1 hr at 258 ml/min with a GE sun lamp to initiate the reaction. Nitrogen was then bubbled through the mixture for 1 hr and the reaction mixture washed with water, twice with 10% sodium bicarbonate, and finally with water. The mixture was dried (MgSO₄) and distilled. The fraction boiling at 124–144° (10 mm), 103 g, was used in the alkylation studies. The assigned composition of this fraction was 1-bromo-1-chloro- (trace), 1-bromo-2-chloro- (0.4%), 1-bromo-3-chloro (3.4%), 1-bromo-4-chloro- (14.7%), 1-bromo-5-chloro- (23.6%), 1-bromo-6-chloro-, and 1-bromo-7-chloro- (54.2%), and 1-bromo-8-chlorooctane (3.4%).

After the alkylation reaction was terminated, the unreacted 1-bromo-3-chloro- and 1-bromo-8-chlorooctane isomers were trapped from a 10 ft × 0.25 in. 20% Carbowax on Chromosorb W column. The nmr¹³ of the former showed two overlapping triplets centered at 3.36 (CH₂Cl) and 3.23 ppm (CH₂Br) and chain methylene groups. The 1-bromo-3-chlorooctane showed nmr bands at 4.00 (t, CHCl), 3.48 (t, BrCH₂), 2.1 (q, BrCH₂CCl-), and 1.7 ppm (m, CH₂CCl), and methylene and terminal methyl protons.

1,1-Dichlorooctane.—Into a 5-l., 3-neck flask was placed 1115 g (5.350 mol) of phosphorus pentachloride and 500 g of benzene. To the stirred slurry was added 600 g (4.7 mol) of octanal over a 5-hr period at no more than 10°. After standing overnight, ice and water were added slowly with cooling. The product was washed with sodium bicarbonate and water and then dried (MgSO₄). The product was distilled; the fraction boiling at 95–99° was found to be 97% pure 1,1-dichlorooctane contaminated with octanal. Since the removal of octanal by sodium bisulfite washes was not successful, the product was redistilled to give 98.6% pure material.

1,1,X-Trichlorooctane.—The chlorination of 1,1-dichlorooctane was performed in the same manner as that used for the preparation of 1-bromo-X-chlorooctane. The fraction boiling at 117–130° (15 mm) was used in the alkylation studies. The composition of this fraction was 1,1,1- (trace), 1,1,2- (2%), 1,1,3- (10.5%),

1,1,4- (16.1%), 1,1,5- (17.9%), 1,1,6- (21.0%), 1,1,7- (23.8%), and 1,1,8-trichlorooctane (10.3%).

After the alkylation reaction was complete, the 1,1,8 isomer and a mixture of the 1,1,2 and 1,1,3 isomers were trapped from a 10 ft × 0.25 in. 20% Carbowax on Chromosorb W column. The nmr of the 1,1,8 isomer showed a triplet at 5.56 (CHCl₂), a triplet at 3.38 (CH₂Cl), a crude quartet at 2.16 (CH₂CCl₂), and methylene protons at 1.37 ppm.

The mixture of 1,1,2 and 1,1,3 isomers, the latter being predominant, showed a pair of overlapping doublets at 5.8, a smaller doublet at 5.71, a complex peak at 3.96, a pair of overlapping doublets at 2.42, methylene protons at 1.3, and terminal methyl at 0.89 ppm. The mixture was then subjected to spin-spin decoupling treatment. Irradiation at 3.9 ppm (a) collapsed the 5.8 ppm band to a triplet, (b) collapsed the 5.71 ppm doublet to a singlet, thereby giving a good indication that the minor constituent was the 1,1,2 isomer, and (c) collapsed the 2.42 ppm doublet pair to one doublet. Irradiation at 2.5 ppm reduced the 5.8 ppm doublets to a singlet and the complex group at 3.96 ppm to a crude triplet. Irradiation at 5.8 ppm did not affect the 3.96 ppm group but reduced the bands at 2.42 ppm to a doublet. C-3 of the 1,1,3 isomer is asymmetric; hence the protons on C-2 are not magnetically equivalent. The assignment of the bands at 5.8 (Cl₂CH), 3.96 (CHCl), and 2.42 ppm (Cl₂CCH₂CCl), and the behavior in the spin-spin decoupling treatment are consistent with that for the 1,1,3 isomer.

1,1,1-Trichlorooctane.—Into a 1-l., stainless steel, stirred autoclave was placed 186 g (1.90 mol) of 1-heptene, 900 g (6.56 mol) of chloroform, and 4.0 g of benzoyl peroxide. The sealed bomb was heated at 80° for 4 hr and a further 8 g of benzoyl peroxide added. The bomb was then heated for another 6 hr at 90°.

This procedure was repeated; the two products were combined. The unreacted chloroform and 1-heptene were removed by distillation, and the bulk of the product distilled at 84–86° (6 mm). More careful fractionation of the 240 g of product so obtained gave a product of 98.5% purity boiling at 85° (6 mm).

1,1,1,X-Tetrachlorooctane.—The chlorination of 1,1,1-trichlorooctane used the previously described procedure. The fraction boiling at 115–123° (6 mm) was used in the alkylation studies. The composition of this fraction was 1,1,1,3- (3.2%), 1,1,1,4- (19.7%), 1,1,1,5- (22.9%), 1,1,1,6- and 1,1,1,7- (46.7%), and 1,1,1,8-tetrachlorooctane (6.3%). The impurities plus the 1,1,1,2 isomer constituted 1.2% of the mixture. Concentration of various isomers, either from distillation cuts before reaction or by trapping the unreactive isomers after reaction, permitted spectroscopic methods to substantiate the assignments. Further, the 1,1,1,3 isomer was synthesized by the addition of carbon tetrachloride to 1-heptene [bp 105–106° (6 mm)].

The nmr of the 1,1,1,3 isomer showed peaks at 4.2 (m, CHCl), 3.18 (eight line distinctive multiplet), 1.82 (m, CClCH₂), 1.4 (methylene protons), and 0.99 ppm (terminal methyl).

The most distinctive feature from the nmr of the 1,1,1,6 isomer was the triplet methyl group at 1.14 ppm. The doublet methyl group of the 1,1,1,7 isomer was observed in the nmr at 1.6 ppm. The nmr of the 1,1,1,8 isomer showed a band at 3.4 ppm (t, ClCH₂) and was distinctive because of the absence of the terminal methyl group.

Alkylation of Benzene with Polyhalooctanes.—Into a 1-l. polyethylene bottle fitted with a stirrer, a gas inlet near the bottom, and a copper condenser, was placed 0.1 mol of the mixed polyhalooctane isomers and 312 g (4 mol) of benzene, and the mixture was cooled to 0°. Liquid hydrogen fluoride, 40 g (2 mol) was added to the stirred, cooled mixture. Boron trifluoride was passed into the stirred mixture throughout the reaction at 4 ml/min. Samples were taken at intervals, at which time the stirring was interrupted. The sample was washed with water, 5% sodium bicarbonate, and water and then dried (MgSO₄).

Samples were analyzed on a 200 ft × 1/16 in. SF 96 coated capillary column. In each series the reactants were analyzed at 140–160° and the column then rapidly heated to 180–200° to permit analysis of the products. The area under the peaks was considered as proportional to weight for isomeric products.

Products. Phenyl-1-bromooctanes.—7-Phenyl-1-bromooctane was trapped from a 10 ft × 0.25 in. 20% Carbowax on Chromosorb W column. The nmr showed aromatic protons at 7.0, a triplet at 3.2 (CH₂Br), a sextuplet at 2.58 (benzylic methine), and methylene protons at 1.2 ppm. The doublet methyl group β to the phenyl group could also be observed at 1.2 ppm but was not separable from the methylene proton signal. The mass spectrum

(11) G. F. Hennion and R. A. Kurtz, [J. Amer. Chem. Soc., **65**, 1001 (1943)] describe the alkylation of benzene with alkyl halides using boron trifluoride and water, alcohol, "or other polar compounds reactive to boron trifluoride" as the catalyst system. The selectivity of primary vs. secondary halides was noted, though yields were less than 70% and reflux temperatures were required.

(12) The effect of variables in the HF/BF₃ system is currently under investigation. Results to date indicate that a certain BF₃ concentration is required before reaction starts.

(13) Nuclear magnetic resonance (nmr) integrals were correct within 5% for assigned structures: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

showed the parent peak at m/e 268, a small peak at 253 ($-\text{CH}_3$), and major peaks at 188 ($-\text{HBr}$), 173 ($-\text{HBr}$, $-\text{CH}_3$), 131 ($\text{C}_{10}\text{H}_{11}^+$), and 105 [$-(\text{CH}_2)_6\text{Br}$].

The phenyl-1-bromooctanes undergo three major modes of cleavage in the mass spectrograph. These are loss of either the alkyl or bromoalkyl group to yield the corresponding benzylic carbonium ions and the loss of both the alkyl group and HBr. Hence there are three distinctive mass spectral peaks associated with each isomer. Those observed are for the 4-phenyl isomer (m/e 211, 131, and 147), the 5-phenyl isomer (225, 145, and 133), the 6-phenyl isomer (239, 159, and 119), and the 7-phenyl isomer. The intensities of the observed peaks were qualitatively appropriate to the assignments made.

The peaks corresponding to the 3-phenyl isomer (m/e 197, 117, and 171) and the 2-phenyl isomer (183, 103, and 185) were not detected by this method or by vpc which would detect 0.1%.

Phenyl-1,1-dichlorooctanes.—7-Phenyl-1,1-dichlorooctane was trapped from the previously described Carbowax column. The nmr showed aromatic protons at 7.0, a triplet at 5.5 (CHCl_2), a sextuplet at 2.58 (benzylic methine), a multiplet at 2.04 (CH_2CCl_2), methylene protons at 1.5, and a doublet at 1.19 ppm (methyl β to phenyl).

The 6-phenyl-1,1-dichlorooctane was concentrated by vpc. The nmr showed aromatic protons at 7.0, a triplet at 5.5 (CHCl_2), a sextuplet at 2.58 (benzylic methine), a multiplet at 2.04 (CH_2CCl_2), methylene protons at 1.5, and a triplet at 0.75 ppm (methyl γ to phenyl).

The mass spectrum of the phenyldichlorooctane mixture showed peaks corresponding to alkyl or alkylidichloro group loss to form the corresponding benzylic carbonium ions and loss of both alkyl group and HCl. The observed peaks corresponded

to the 4-phenyl isomer (m/e 201, 147, and 165), the 5-phenyl isomer (215, 133, and 179), the 6-phenyl isomer (229, 119, and 193), and the 7-phenyl isomer (243, 105, and 207).

Phenyl-1,1,1-trichlorooctane.—The 7-phenyl isomer was recognized by the characteristic doublet at 1.15 ppm in the nmr. The mass spectrum showed the parent peak at m/e 292 and peaks at 256 ($-\text{HCl}$), 241 ($-\text{HCl}$, $-\text{CH}_3$), 131 ($\text{C}_{10}\text{H}_{11}^+$), and 105 [$-(\text{CH}_2)_6\text{CCl}_3$].

The 6-phenyl isomer showed a triplet in the nmr at 0.7 ppm characteristic of a methyl group γ to phenyl. The mass spectrum showed the parent peak at m/e 292 and peaks at 256 ($-\text{HCl}$), 227 ($-\text{HCl}$, $-\text{C}_2\text{H}_5$), 145 ($\text{C}_{11}\text{H}_{13}^+$), and 119 [$-(\text{CH}_2)_6\text{CCl}_3$].

The mass spectrum of the phenyl-1,1,1-trichlorooctane mixture showed peaks corresponding to the 5-phenyl isomer (m/e 249, 133, and 213) and the 4-phenyl isomer (235, 147, and 199).

The nmr of all isomers showed the $-\text{CH}_2\text{CCl}_3$ peak overlapping with the methine hydrogen.

Registry No.—Benzene, 71-43-2; 1,1-dichlorooctane, 20395-24-8; 1,1,1-trichlorooctane, 4905-79-7; 1,1,1,3-tetrachlorooctane, 18088-13-6; 1,1,1,6-tetrachlorooctane, 20414-34-0; 1,1,1,7-tetrachlorooctane, 20414-35-1; 1,1,1,8-tetrachlorooctane, 10311-13-4; 7-phenyl-1,1-dichlorooctane, 20414-37-3; 6-phenyl-1,1-dichlorooctane, 20414-38-4; 7-phenyl-1,1,1-trichlorooctane, 20414-39-5; 6-phenyl-1,1,1-trichlorooctane, 20414-40-8; 1,1,8-trichlorooctane, 20414-41-9; 1,1,3-trichlorooctane, 4905-80-0.

Application of the Linnett Electronic Theory to Organic Chemistry.

II. Introduction

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The double-quartet theory of Linnett is shown to account for a wide variety of typical organic structural phenomena. The concept of L strain, a unique corollary of the Linnett theory, is discussed and put on a semiquantitative basis. Examples of problems in geometry, stabilization, hyperconjugation, and configurational inversion are provided from among the classes alkanes, alkenes, alkynes, amines, carbanions, carbonium ions, radicals, and carbenes, and certain predictions are made.

In the past few years there has appeared a modified theory of chemical binding, developed by Linnett.^{1,2} Based on the principles of quantum mechanics, Linnett's theory nevertheless differs drastically in many cases from that held in recent decades by most chemists (the Lewis-Langmuir octet rule),³⁻⁵ while in other cases it agrees. Heretofore the chief area of application has been in inorganic chemistry with a few ventures into organic territory.

We have found that a detailed examination of structure and mechanism throughout organic chemistry in the light of the Linnett concepts can provide increased understanding. A portion of this work has already been presented in preliminary form.⁶ In this paper, which is intended as the introduction to a series of detailed surveys of mechanism, Linnett's structural concepts are extended, in the simplest possible way, to typi-

cal organic molecules and intermediates. For the most part, discussions will be limited to elements of atomic number below neon in the periodic table.

The Linnett Theory.—Inasmuch as a complete description has been published,^{1,2} only a few points will be repeated here. The principal innovation is the treatment of the outermost shell of electrons around the nucleus of an atom as an array, not of pairs with perhaps an odd electron, but of two spin sets, one of each spin. The disposition of the electrons in each spin set toward each other is rather firmly fixed, owing both to the Pauli principle and their mutual electrostatic repulsion, at that with the maximum mutual distance within the radius of the shell. (By the "position" of an electron, of course, "most probable position" is meant throughout.) Thus, a quartet occupies the corners of a regular tetrahedron, a trio the corners of an equilateral triangle, and a duo the ends of a straight line, all centered on the nucleus. The relative positions of the two spin sets are the most staggered possible (consistent with the maximization of binding energy), to minimize interelectronic repulsion. The second restriction is weaker than the first, however, because the Pauli principle is not involved.

(1) J. W. Linnett, *J. Amer. Chem. Soc.*, **83**, 2643 (1961).

(2) J. W. Linnett, "The Electronic Structure of Molecules," Methuen & Co. Ltd., London, 1964.

(3) G. N. Lewis, *J. Amer. Chem. Soc.*, **38**, 762 (1916).

(4) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, N. Y., 1923.

(5) I. Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221 (1916).

(6) R. A. Firestone, *Tetrahedron Lett.*, 971 (1968).