The data in Table V show that, in the reaction (transalkylation) of the 1,3,5-triethylbenzene and ethylbenzene, the amount of the *m*-diethylbenzene was greater than that of the 1,2,4-triethylbenzene. This indicates that *m*-diethylbenzene was the precursor of this latter compound in this reaction. The diethylbenzene fraction was initially richer in the *meta* isomer than the final equilibrium distributions of 1:12:6, *ortho–meta–para*, since it is the only product of the dealkylation of the 1,3,5 compound as indicated in eq 4. The products obtained from the transfer of an ethyl group to the ethylbenzene reactant should be in equilibrium distribution, which is again richer in the *meta* isomer. The experimental results support these conclusions within the accuracy of the analytical measurements.

That the 1,2,4-triethylbenzene has not previously been reported[4,13] as one of the products of transalkylation using metallic halide catalysts is simply explained by the greater stability of catalyst complexes of *meta* derivatives. For example, the equilibrium leading to the formation of the 1,3,5-triethylbenzene as shown in eq 5 is shifted far to the right,[13] particularly when large, noncatalytic amounts of Lewis acid catalysts are employed.

$$(1,2,4\text{-Et}_3\text{C}_6\text{H}_3 \cdot \text{H})^+ \cdot \text{BF}_4^- \rightleftharpoons 1,2,4\text{-Et}_3\text{C}_6\text{H}_3 \rightleftharpoons$$

$$1,3,5\text{-Et}_3\text{C}_6\text{H}_3 \rightleftharpoons (1,3,5\text{-Et}_3\text{C}_6\text{H}_3 \cdot \text{H})^+\text{BF}_4^- \quad (5)$$

The product distributions of both the isomerization and transalkylation reactions always agree with calculated thermodynamic equilibria with the molecular sieve zeolite catalyst. This indicates the absence of the stable catalyst–reactant intermediate complex frequently observed with conventional acid catalysts.

Experimental Section

The di- and triethylbenzenes were obtained from the Aldrich Chemical Co., Milwaukee, Wis., and were used without further purification. The *o*-diethylbenzene contained 93% *ortho*, 6% *meta*, and 1% *para;* the *m*- and *p*-diethylbenzenes and the 1,3,5-triethylbenzene were all 99% pure.

The reactions were carried out in a 100-ml flask, fitted with a water-cooled condenser and a magnetic stirrer. The crystalline catalyst was synthesized from Type Y zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5.0 by partial multivalent cation exchange (40% Ce^{3+}) and partial decationization (50%). The balance of the cations was sodium. The preparation and pertinent properties of this material have been previously reported.[6] Five grams of catalyst were used/0.5 mol of reactant and the reaction temperatures were maintained using a constant-temperature oil bath. Samples were removed periodically and analyzed on a Perkin-Elmer 154 D vapor fractometer. The fractometer was equipped with a 150-ft *m*-bis(*m*-phenoxyphenoxy)benzene-coated (modified by 20% Apiezon L) capillary column and a hydrogen flame ionization detector. The 1,2,4-trialkylbenzene was characterized by both ir and uv analyses.

Retention times of ethylbenzene, diethylbenzenes, and triethylbenzenes are given in Table VI.

TABLE VI

RETENTION TIMES OF ETHYLBENZENE, DIETHYLBENZENES, AND TRIETHYLBENZENES

Compd	Retention time,[a] min
Ethylbenzene	3.7
o-Diethylbenzene	5.8
m-Diethylbenzene	5.5
p-Diethylbenzene	5.6
1,2,4-Triethylbenzene	11.2
1,3,5-Triethylbenzene	10.0

[a] At 150°; He, 30 psi.

Registry No.—Ethylbenzene, 100-41-4; *o*-diethylbenzene, 135-01-3; *m*-diethylbenzene, 141-93-5; *p*-diethylbenzene, 105-05-5; 1,2,4-triethylbenzene, 877-44-1; 1,3,5-triethylbenzene, 102-25-0.

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(13) A. P. Lien and D. A. McCauley, *J. Amer. Chem. Soc.*, **75**, 2407 (1953).

Long-Range Effects in the Alkylation of Benzene with Dichloroalkanes[1]

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The results obtained from alkylation reactions on benzene with two series of primary chloro-containing dichloroalkanes are interpreted on the basis of a long-range effect of the reference primary chloro group on the reaction of the second chloro group. Benzene was alkylated with 1,X-dichlorooctane (*i.e.*, a mixture of the 1,1 through 1,8 isomers) using a boron trifluoride–hydrogen fluoride catalyst (a system specific for alkylation of secondary halides). The relative reaction rates for the 1,3, 1,4, 1,5, 1,6, and 1,7 isomers and the composite rate for the secondary monochlorooctanes were 1, 9.9, 23.2, 36.8, 49, and 73, respectively. The products were 7-, 6-, 5-, and 4-phenyl-1-chlorooctanes in a ratio 53:29:14:4, which was independent of the degree of dichloride conversion. The 1,1, 1,2, and 1,8 isomers did not react. The aluminum chloride catalyzed alkylation of benzene with a series of α,ω-dichloroalkanes was also examined. The rate of reaction was in the order of 1,4-dichlorobutane > 1,6-dichlorohexane > 1,5-dichloropentane > 1,3-dichloropropane and was generally slower than that of 1-chlorohexane. The higher members of this series gave the greatest amount of rearranged products from the initial reaction, but this was always less than the corresponding 1-chloroalkane. 1,4-Dichlorobutane is a special case in which anchimeric assistance by one chloro group in the ionization of the other is responsible for an increased reaction rate.

In our previously reported work on the alkylation of benzene with 1,2-dichloroalkanes using aluminum chloride, it was observed that the adjacent primary chloride had a profound effect in determining the products of reaction.[2] This report describes our work on systems in which the two chloro groups are farther apart. We have studied the effect of one chloro group on the reaction rate and products from reaction of the second chloro group. Special emphasis has been placed on the change of the effect with distance between the two chloro groups and on a comparison with the monochloroalkane reaction. Two alkylation systems have been used in this work. The alkylation of benzene with

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(1) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) D. L. Ransley, *J. Org. Chem.*, **31**, 3595 (1966).

1,X-dichlorooctane[3] using a hydrogen fluoride–boron trifluoride catalyst has been examined. Further, the aluminum chloride catalyzed alkylation of benzene with a series of α,ω-dichloroalkanes has been studied and compared with similar reactions of 1-chloroalkanes.

I. The Alkylation of Benzene with 1,X-Dichlorooctane.—The radical chlorination of 1-chlorooctane was taken to about 20% conversion in order to maximize the amount of dichlorooctane. The dichlorooctane fraction, when analyzed by vapor phase chromatography (vpc), showed the presence of eight compounds in the ratio 2.0:5.7:12.2:16.9:17.8:18.6:20.6:4.9.[4,5] These were presumed to be the 1,1 through 1,8 isomers, respectively.

Although it has been claimed[5] that the isomers elute from "boiling point" columns (such as the one used in this work) in order of increasing distance between the chloro groups, we wished to verify this observation.[6] The 1,1, 1,2, 1,4, 1,5, and 1,8 isomers were either synthesized or purchased. These isomers did, indeed, elute in "numerical order," and did correspond to the first, second, fourth, fifth, and eighth peaks, respectively. It therefore, seemed reasonable to assume that the third peak was the 1,3 isomer and the sixth and seventh peaks were the 1,6 and 1,7 isomers.

The alkylation of benzene was carried out by adding 2 mol of liquid hydrogen fluoride to a cold solution of 0.2 mol of 1,X-dichlorooctane in 4 mol of benzene. Boron trifluoride was bubbled through the well-stirred mixture at about 4 ml/min at 0°.

Under these conditions, the 1,1, 1,2, and 1,8 isomers did not react. This was demonstrated by the addition of external vpc standards. Hence, the 1,1, 1,2, and 1,8 isomers (together with the 1% 1-chlorooctane contaminant) could be used as internal vpc standards.

No reaction occurred for the first 30–35 min. The reaction then proceeded smoothly, although the reaction rates were different for each isomer. The rates of reaction for the various isomers were in the order 1,7 > 1,6 > 1,5 > 1,4 > 1,3.

The products of reaction were identical and showed identical distribution in each sample taken at various time intervals throughout the reaction. The products were 7-, 6-, 5-, and 4-phenyl-1-chlorooctane in the approximate ratio 53:29:14:4.

The reaction of each dichlorooctane isomer was shown to be first order in dichloride in the presence of excess benzene and hydrogen fluoride. The accuracy of the kinetic measurements for the 1,6 and 1,7 isomers was not great for these rather fast reactions. It was convenient to compare the log $([\mathrm{RCl_2}]_0/[\mathrm{RCl_2}]_t)$[7] values for each isomer in each sample of several runs in order to establish a relative rate scale for the reactive isomers. Taking the rate constant for the 1,3 isomers ($k_{1,3}$) as unity, we observed $k_{1,3} = 1$, $k_{1,4} = 9.9$, $k_{1,5} = 23.2$, $k_{1,6} = 36.8$, $k_{1,7} = 49$.

The same reaction was run in competition with a mixture of 1-, 2-, 3-, and 4-chlorooctanes[8] (the 1-chlorooctane not reacting). In an example the first-order rate constants (sec^{-1}) obtained by direct measurement were $k_{\mathrm{mono}} = 5.8 \times 10^{-3}$, $k_{1,7} = 4.1 \times 10^{-3}$, $k_{1,6} = 2.92 \times 10^{-3}$, $k_{1,5} = 1.73 \times 10^{-3}$, $k_{1,4} = 7.95 \times 10^{-4}$, $k_{1,3} = 7.12 \times 10^{-5}$, the very slight (but detectable) rate differences of the isomeric monochlorooctanes being ignored, a composite value being used in this study.

Further control reactions were also run. The reaction of 1,5-dichlorooctane alone was shown to be first order in dichloride and gave the same products and distribution as did 1,X-dichlorooctane. No isomerization of the dichlorooctane occurred prior to alkylation.

A mixture of 7-, 6-, 5-, and 4-phenyl-1-chlorooctane (37.9, 36.7, 20.5, and 5.0%, respectively) was subjected to the reaction conditions, but the rate of isomerization was very slow.

The reaction of a 1-, 2-, 3-, and 4-chlorooctane mixture or of 2-chlorooctane yielded identical products for reactions of equal duration. However, gradual product isomerization from 29.6, 34.3, and 36.2% of 2-, 3-, and 4-phenyloctane initially to 39.6, 31.8, and 28.6%, respectively, after 6.5 hr was observed.

II. The Alkylation of Benzene with α,ω-Dichloroalkanes.—The aluminum chloride catalyzed alkylation reactions of benzene with 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, and 1,6-dichlorohexane have been studied. Product distribution and rate characteristics have been examined and compared with similar reactions of 1-chloroalkanes.

The products from the reactions of the dichloroalkanes are readily predictable from previous studies of these or similar[2,9] systems or the corresponding dibromides.[10] The reactions were carried out with 5 mol % aluminum chloride at 0–5° in excess benzene for 2 hr. The product distribution for each reaction is shown in Chart I.

The products are formed *via* an initial reaction which proceeds without rearrangement (path A, Chart I) or with rearrangement (path B). Computation of the amount of product formed *via* path A (as opposed to path B) is complicated by the subsequent reactions of the initially formed phenylchloroalkanes. Further examination of the reactions of these compounds under similar conditions was undertaken. It was assumed that the phenylchloroalkanes would behave as reactants in the same manner as when formed in the α,ω-dichloroalkane reactions. Therefore, one may proportionate the products between paths A and B.

3-Phenyl-1-chloropropane (I) gave the diphenylpropanes, III, IV, and V, in the ratio 23.5:72.2:4.3. Since I yields 23.5% III and 4.3% V while forming 72.2% IV, it is inferred that 16.0% III and 3.0% V[11] would be formed *via* path A during formation of 51.8% IV. 5-Phenyl-1-chloropentane (XII) was isolated from the reaction of 1,5-dichloropentane and its behavior under alkylation conditions examined on a small scale. Approximately the same amount of XIV as the

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(3) X indicates a chloro group on each carbon, *i.e.*, a mixture of 1,1-, 1,2-, . . ., and 1,8-dichlorooctane isomers.

(4) Before distillation the ratio of products was 2.0:6.1:11.8:15.6:16.8:18.5:19.8:9.4. This is slightly, but significantly, at variance with the work of Colebourne and Stern.[5]

(5) N. Colebourne and E. S. Stern, *J. Chem. Soc.*, 3599 (1965).

(6) Colebourne and Stern[5] isolated the isomers by preparative vpc and used nmr to distinguish between the isomers. It was not clear to us how, for instance, 1,4- and 1,5-dichlorooctane could be readily distinguished by nmr.

(7) $[\mathrm{RCl_2}]_0$ = dichloride (or monochloride) concentration at time zero; $[\mathrm{RCl_2}]_t$ = dichloride concentration at time *t*.

(8) Obtained by monochlorination of *n*-octane.

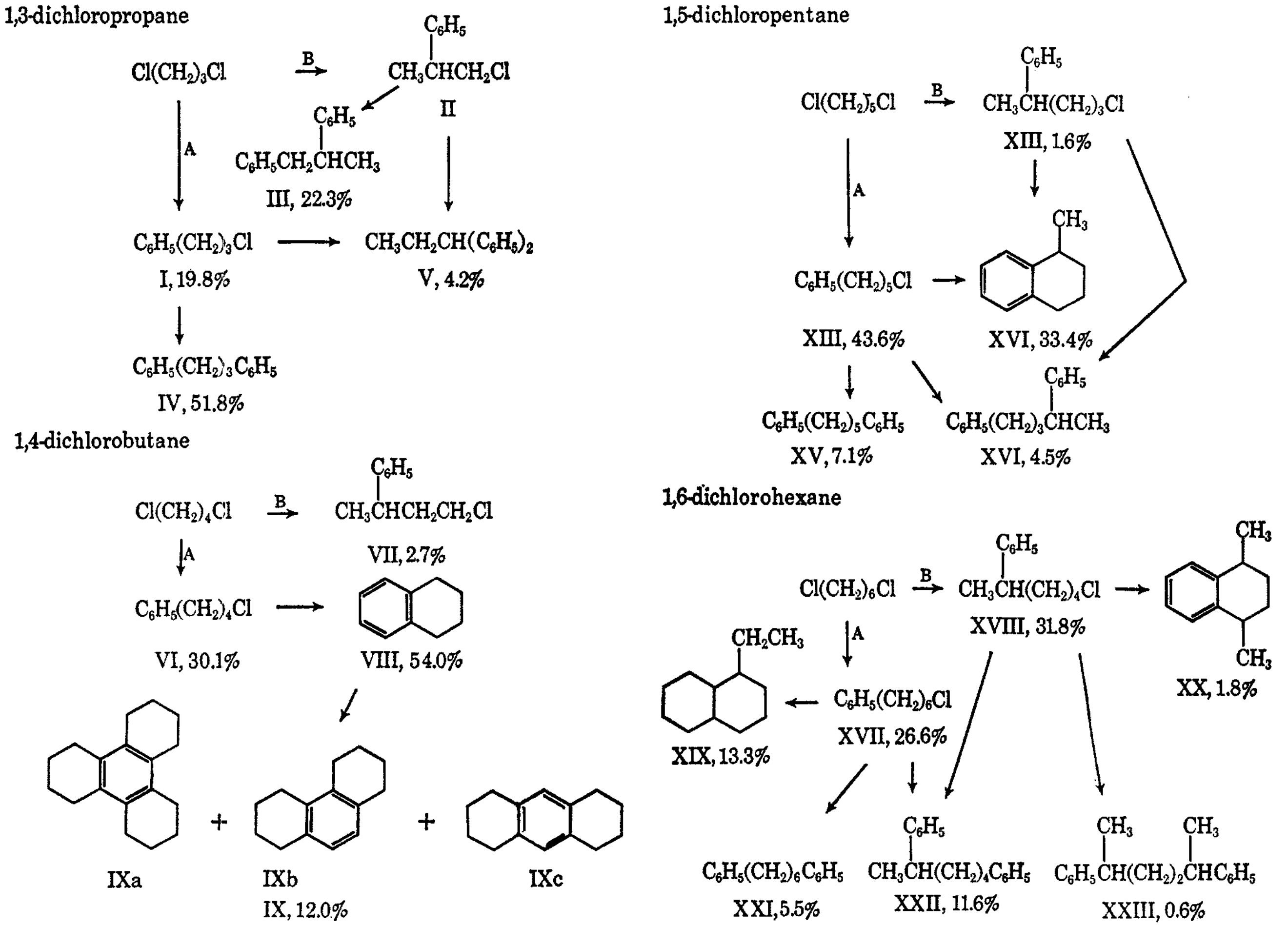
(9) K. M. Shadmanov, *Dokl. Akad. Nauk Uz. SSR*, No. 11, 37 (1957); *Chem. Abstr.*, **53**, 5214*f* (1959).

(10) H. Nozaki, M. Okazaki, N. Yamae, Y. Nishikawa, T. Hisida, and K. Sisido, *J. Org. Chem.*, **30**, 1303 (1964).

(11) 51.8/72.2 × 22.3 = 16.

CHART I

PRODUCTS FROM THE ALKYLATION OF BENZENE WITH α,ω-DICHLOROALKANES



sum of diphenylpentanes XV and XVI was formed. This would suggest that all XV and XVI were formed *via* path A. This is consistent since the closure of 4-phenyl-1-chloroalkanes is known to proceed with ease[2,12] and with little diphenylalkane formation. Compound XVII yielded 36.4% XIX, 31.4% XXI, and 25.5% XXII. The conclusion is that 2% XXII is formed *via* path A.

In Table I there is listed the proportion of products formed *via* paths A and B which is also compared with the amount of unrearranged (i.e., amount of 1-phenylalkane) and rearranged product from the identical reaction of the corresponding 1-chloroalkane.

Attempts were made to compare the rates of reactions of the dichloroalkanes with that of the monochloralkanes. However, the early experiments showed no reactions to which any kinetic order could be assigned. It appeared that there was gradual deactivation of the catalyst throughout each run. The deactivation effect was not the same for each reactant. It is possible that the catalyst is deactivated by complexing with the reaction products thereby accounting for the difference in degree of the deactivation effect.

Competition rate studies were then examined. To facilitate analysis 1-chlorohexane was used as the standard monochloroalkane, and any small differences between the C_3, C_4, C_5, and C_6 chloroalkanes were neglected. The competition reactions of 1-chlorohexane with each dichloroalkane were carried out separately and with a mixture of all four dichloroalkanes. In each reaction it was observed that the ratio of the log $[RCl_2]_0/[RCl_2]_t$[7] function remained constant throughout the run. The treatment given, therefore, was that of a reaction first order in dichloroalkane (or monochloroalkane), the deviation being ascribed to catalyst deactivation. In this manner an estimate for the relative first-order rate constants was achieved. Setting the first-order rate constant ($k_{1,3}$) for the 1,3-dichloropropane reaction as unity, the relative rates were $k_{1,3} = 1$, $k_{1,4} = 108$, $k_{1,5} = 24$, $k_{1,6} = 45$, $k_{\text{mono}} = 50$.

TABLE I

REARRANGEMENT IN THE ALKYLATION OF BENZENE WITH MONO- AND DICHLOROALKANES

Reactant	Products,[a] wt % Path A unrearranged	 Path B rearranged	 Ambiguous
1-Chloropropane	44.4	55.6	
1,3-Dichloropropane	90.6[b] (71.6)	7.5 (0.0)	1.9 (28.4)
1-Chlorobutane	36.0	60.6	
1,4-Dichlorobutane	96.1[c] (96.1)	2.7 (2.7)	1.2 (1.2)
1-Chloropentane	40.5	59.5	
1,5-Dichloropentane	66.8[d] (50.7)	23.4 (1.6)	9.8 (47.7)
1-Chlorohexane	32.5	67.5	
1,6-Dichlorohexane	47.4[e] (45.4)	49.8 (39.6)	2.8 (15.0)

[a] Figures in parentheses show results when subsidiary phenylchloroalkane experiments are ignored. [b] I, 19.8%; IV, 51.8%; III, 16.0%; V, 3.0%: total 90.6%. [c] VI, 30.1%; VIII, 54.0%; IX, 12.0%: total 96.1%. [d] XII, 43.6%; XV, 7.1%; XIV, 11.6%; XVI, 4.5%: total 66.8%. [e] XVII, 26.6%; XIX, 13.3%; XXI, 13.3%; XXU, 5.5%; XXII, 2.0%: total 47.4%.

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[12] A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).

The value given for $k_{1,3}$ is little more than an estimate, owing to the errors introduced by competition experiments with reactants with vastly different rates.

Discussion

In this work an attempt has been made to isolate the effect of a primary chloro group on the reaction of a second chloro group in the same molecule. Particular emphasis has been placed on the effect as a function of the number of carbons separating the two chloro groups.

It may be observed that in both systems the rate of reaction of dichloroalkanes increases as the distance between the two chloro groups is increased but is slower than the corresponding monochloroalkane. The exception to these generalizations is the reaction of 1,4-dichlorobutane.

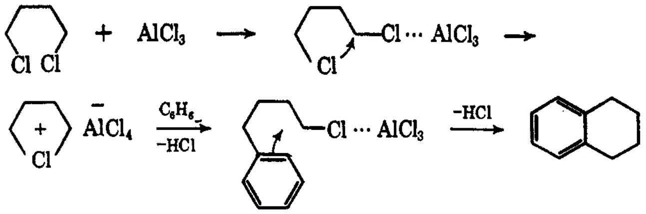
In the HF–BF_3-catalyzed reactions, the products from 1,X-dichlorooctane show a strong tendency for phenyl attachment at secondary positions most distant from the unreactive primary chloride. In contrast, the monochloroalkanes form products with random phenyl attachment to the secondary carbons.

The α,ω-dichloroalkanes undergo initial reaction with less rearrangement than the corresponding monochloroalkanes, the difference decreasing as the distance between the chloro groups is increased.

These generalized observations may be interpreted as being due to an electron-withdrawing influence of the reference primary chloro group on the reaction of the other chloro group. As the distance between the two chloro groups is increased, the influence is decreased.

The alkylation reaction involves ionization of a chloro group with generation of at least a partial positive charge. This would be a higher energy process in the presence of an electron-withdrawing influence. Rearrangement in reactions of the α,ω-dichloroalkanes would necessitate transfer of at least a partial positive charge to a carbon closer to the unreacted chloro group. This process would also be energetically less favorable when the influence of the chloro group is stronger. In contrast, rearrangement away from the primary chloro group in the reaction of 1,X-dichlorooctane is favorable. By this process the destabilizing influence of the unreactive primary chloride is decreased.

The reaction of 1,4-dichlorobutane is considered to be a special case. This reaction does not fit into the general pattern of a gradual rate change in the α,ω-dichloroalkane series. Further, the reaction rate is faster than the primary monochloroalkane and gives less rearranged product than would be anticipated on the basis of the above interpretation. It is believed that ionization of 1,4-dichlorobutane occurs with anchimeric assistance of the remaining chloro group, thereby generating a five-membered cyclic chloronium ion.[13-16] After alkylation on benzene the favored phenyl participation[2] in ionization of the remaining chloro group assists in maximizing the amount of product formed *via* the unrearranged route. This sequence may be pictured as shown.



Evidence for similar chloronium ion formation has been demonstrated by Peterson.[13-16]

It is observed that 1,6-dichlorooctane reacts more slowly than the secondary monochlorooctanes and that 1,6-dichlorohexane reacts more slowly than 1-chlorohexane and gives less rearranged products. It is therefore apparent that the influence of the reference primary chloro group is effective at least six methylene groups removed from the reaction site.

The closest analogies to this observation are the studies of Peterson and his coworkers[15] and of Stevenson and Williamson.[17] Peterson observed that there was a gradual change in reaction rate for the addition of trifluoroacetic acid to $Cl(CH_2)_nCH{=}CH_2$ as n is increased. He observed that the chloro group has an influence at distances 11 carbons removed, although he attributed the magnitude of this influence to be a facet of his particular system. Stevenson and Williamson observed a gradual change in pK for a series of cyanoamines, with the functional groups separated by as many as five methylene groups.

Both of these groups of workers interpret their results as due to a long-range inductive effect of the chloro and the cyano group, respectively. As a test of their theory they plot log ($\log F_u - \log F_s$) (where F_u = the function for the unsubstituted case and F_s for the substituted case) against the number of methylene groups separating the substituent from the critical reaction site. This treatment has been widely discussed and largely accepted.[13-26] Both research groups find linear correlations. An attenuation factor for the change in the effect per methylene may therefore be reached. Attenuation factors of 0.3 to 0.55[18-28] have been previously used or calculated. Stevenson and Williamson find 0.5 to be the attenuation factor and Peterson 0.65.

A similar treatment may be used for the rates of reaction of the 1,X-dichlorooctane series. A good linear plot was obtained using the data for the monochlorooctane and the 1,3-, 1,4-, 1,5-, 1,6-, and 1,7-dichlorooctanes.[29] The attenuation factor was found to be 0.58.

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(18) C. G. Derick, *ibid.*, **33**, 1181 (1911).

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(25) J. C. McGowan, *J. Appl. Chem.*, **10**, 312 (1960).

(26) R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 592.

(27) M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949); 2329 (1950).

(28) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

(29) There is no evidence for anchimeric assistance in the reaction of 1,4-dichlorooctane. In this case there is probably association of the excess hydrogen fluoride with the primary chloro group. In this way the unshaved electrons are not available for participation in the ionization of the secondary chloro group. The behavior of 1,4-dichlorobutane is different because of the presence of only catalytic amounts of aluminum chloride.

Similarly, the same treatment could theoretically be applied to the α,ω-dichloroalkane series. However, the accuracy of the data is not great and provides only a three-point plot. That a linear plot is not obtained cannot be taken as being very meaningful.

Such studies as the one presented here inevitably have a bearing on the controversial question of the mechanism of transfer of the effect of the chloro group. The case for the mechanism being due to a field effect has been presented by Dewar.[30] The arguments for a purely inductive transfer apparently is more acceptable to many chemists.[13–28] The value of the Kirkwood–Westheimer[31] treatment of the first and second dissociation constants of saturated dicarboxylic acids cannot be discounted. Further, more recent investigations have explained long-range effects as field effects[32] or have detected negligible inductive effects for groups separated by more than two carbon atoms.[33,34]

Until a reliable quantitative treatment of field effects has been developed, the dispute will remain. Although long-range effects have been adequately demonstrated in our systems, the mode of transfer of the influence cannot be decided upon on the basis of our work.

Experimental Section

Benzene was stirred thoroughly twice with 5 wt % concentrated sulfuric acid and washed with water, 10% sodium bicarbonate, and water. After partially drying over magnesium sulfate the benzene was refluxed with and then distilled from calcium hydride immediately before use.

1,X-Dichlorooctane.—Into a 1-l. turbomixer, fitted with a gas inlet at the bottom and with a water-cooled condenser, was placed 561 g (3.77 mol) of 1-chlorooctane. Nitrogen was passed through the solution for 15 min and then chlorine was passed at approximately 443 ml/min for 36 min with a sun lamp to cause initiation. After flushing with nitrogen for 30 min, the reaction mixture was washed with water, 10% sodium bicarbonate, water, and dried over magnesium sulfate. The product was distilled through a 9 in. × 1 in. column packed with glass helices; the portion boiling at 112–119° (15 mm) was used in our work.

This material, after distillation, was analyzed on a 200 ft × $^1/_{16}$ in. SF-96 coated capillary column in a Perkin-Elmer 800 chromatograph at 110°. Under these conditions the composition for the 1,1- through 1,8-dichlorooctane, in order, was 2.0, 5.7, 12.2, 16.9, 17.8, 18.6, 20.6, and 4.9%; and the relative retention times in minutes were 9.9, 10.5, 11.4, 12.4, 13.3, 14.2, 14.5, and 18.5, respectively. The product contained 1.2% 1-chlorooctane.

The 1,1, 1,2, 1,4, 1,5, and 1,8 isomers were identified by spiking with authentic materials prepared as follows.

1,1-Dichlorooctane.—The product from the reaction of 1-octanal with phosphorus pentachloride had a 9.9-min retention time.

1,2-Dichlorooctane.—The addition of chlorine to 1-octene with stannic chloride as catalyst gave a product with a 10.5-min retention time.

1,4-Dichlorooctane.—Treatment of γ-octanoic lactone with lithium aluminum hydride yielded a compound which upon treatment with thionyl chloride and pyridine gave a product with a 12.4-min retention time.

1,5-Dichlorooctane.—The hydration of dihydropyran to α-hydroxytetrahydropyran was followed by salting out with potassium carbonate and ether extraction. The dry ether solution, when treated with more than a 2 mol equiv of *n*-propylmagnesium bromide, yielded a compound[35] which, after treatment with thionyl chloride and pyridine, yielded a material with a 13.3-min retention time.

1,8-Dichlorooctane.—Aldrich Chemical Co. 1,8-dichlorooctane had a retention time of 18.5 min.

The products of these reactions and the intermediates gave nuclear magnetic resonance (nmr) spectra consistent with their structures.

Alkylation of Benzene with 1,X-Dichlorooctane.—Into a 1-l. polyethylene bottle fitted with a mechnical stirrer, gas inlet tube, and sampling port was placed 0.2 mol of 1,X-dichlorooctane and 312 g (4 mol) of benzene. The mixture was cooled in ice and 40 ml of liquid hydrogen fluoride added. To the stirred, cooled mixture was added boron trifluoride gas at about 4 ml/min below the surface of the mixture. Samples were taken at various time intervals by pipet after stirring was momentarily interrupted to permit the hydrogen fluoride to settle. Each sample was washed with water, dilute potassium hydroxide, and water and then dried over magnesium sulfate.

Identification of Products from Reaction of 1,X-Dichlorooctane. 7-Phenyl-1-chlorooctane showed nmr[36] bands at 3.32 (t), 2.61 (q), 1.59 (m), and 1.2 (d). Mass spectrum showed parent peak at 224 and a major peak at 105. Infrared showed primary chloride and monosubstituted phenyl.

6-Phenyl-1-chlorooctane showed nmr bands at 3.32 (t), 2.35 (m), 1.59 (m), and 0.76 (t). Mass spectrum showed parent peak at 224, a major peak at 119, and a smaller peak at 195.

4-Phenyl-1-chlorooctane.—The products from the reaction of 1,X-dichlorooctane were treated with 3 wt % aluminum chloride at 0° for 10 min. The 4-phenyl-1-chlorooctane was completely eliminated having been converted with a small amount of the 5-phenyl-1-chlorooctane, into 1-butyltetralin and *cis*- and *trans*-1-propyl-3-methyl tetralin. The ready closure of 4-phenyl-1-chloroalkanes to tetralins has been well established.[2,12] The 6- and 7-phenyl-1-chlorooctanes remained essentially unchanged.

Mass spectral analysis of the mixture showed a parent peak at 224 and peaks at 209 ($-CH_3$), 195 ($-CH_3CH_2$), 181 ($-CH_3CH_2CH_2$), 167 ($-CH_3CH_2CH_2CH_2$), 147 ($-(CH_2)_3Cl$), 133 ($-(CH_2)_4Cl$), 119 ($-(CH_2)_5Cl$), and 105 ($-(CH_2)_6Cl$). This accounts for all major peaks above 100 with exception of one at 159 (not chlorine containing) and a small one at 188 (possibly chlorine containing). In qualitative fashion this analysis bears out the assignments given.

Alkylation of Benzene with α,ω-Dichloroalkanes.—Into a 500-ml, three-necked flask fitted with a stirrer, thermometer, and drying tube was placed 0.3 mol of the dichloride in 300 ml of benzene. The stirrred mixture was cooled in ice; then 2 g (0.015 mol) of aluminum chloride was added in one portion. A mild exotherm ensued, but the over-all reaction temperature was 5 ± 3°. After 2 hr the reaction was terminated by the addition of cold 5% hydrochloric acid. The organic phase was washed with water, dilute sodium bicarbonate, and water before drying over magnesium sulfate.

Analyses were performed on a 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W column in an A 350 Aerograph chromatograph. After solvent removal under reduced pressure, larger samples were injected into the column and the major components were trapped and identified by spectroscopic methods.

Product Identification. From 1,3-Dichloropropane.—Product I was identical with the purchased authentic material (Eastman Chemical Co.). Product IV showed nmr[36] bands at 2.42 (t) and 1.85 (q); mass spectral (ms) parent peak at 196; correct infrared (ir) spectrum. Product III and V were identical with products previously reported.[2]

From 1,4-Dichlorobutane.—Product VI showed nmr bands at 3.39 (t), 2.56 (t), and 1.72 (m); ms peak at 168; ir showed monosubstituted phenyl and primary chloride. Product VII showed nmr bands at 3.2 (m), 1.9 (m), and 1.22 (d); ms parent peak at 168, major peak at 105, peak at 153; ir showed monosubstituted phenyl and primary chloride. Product IXa (dodecahydrotriphenylene) showed nmr bands at 2.25 (s) and 1.7 (s); uv 272 mμ; ms parent peak 240; ir identical with that previously reported.[37] Product VIII was identical with authentic material.

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[37] "Catalog of Infrared Spectra Data," American Petroleum Institute Research Project-44, Chemical Thermodynamics Center, Texas A & M, College Station, Texas, Serial No. 2267.

From 1,5-Dichloropentane.—Product XII showed nmr bands at 3.33 (t), 2.52 (t), and 2.6 (m); ms parent peak at 182; ir showed monosubstituted phenyl and primary chloride. Product XIII showed nmr bands at 3.32 (t), 2.58 (m), 1.63 (m), and 1.22 (d); ms parent peak at 182, large 105 peak, 167 peak; structure confirmed by ir. Products XIV and XV had ir spectra identical with those previously reported;[9] ms and nmr were consistent. Product XVI showed nmr bands at 2.47 (m), 1.5 (m), and 1.18 (d); ms parent peak at 224, 209 peak; it was consistent.

From 1,6-Dichlorohexane.—Product XVII was identical with purchased material (Ash Stevens Co.). Product XVIII showed nmr bands at 3.3 (t), 2.55 (q), 1.56 (m), and 1.17 (d); ms parent peak at 196, 181 peak; ir showed monosubstituted phenyl. Products XXI, XIX, and XX had ir spectra identical with those previously reported;[10] nmr and ms were consistent.

Registry No.—Benzene, 71-43-2; 7-phenyl-1-chlorooctane, 15733-57-0; 6-phenyl-1-chlorooctane, 15733-58-1; III, 1081-75-0; VI, 4830-93-7; VII, 13556-61-1; IXa, 1610-39-5; XII, 15733-63-8; XIII, 15733-64-9; XVI, 6443-80-7; XVIII, 13556-57-5.

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II. Solvent Effects in the Alkylation of Benzene with 1-Dodecene and *trans*-6-Dodecene in the Presence of Aluminum Chloride

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1-Dodecene and *trans*-6-dodecene alkylate benzene in the presence of aluminum chloride–hydrogen chloride at 35–37° to give similar isomer distributions of phenyldodecanes. At that temperature the alkylation reaction is accompanied by isomerization of the products to a certain equilibrium distribution that is different from the isomer distribution in the absence of product isomerization. Alkylation at 0° or below suppresses product isomerization and results in an isomer distribution that depends on the position of the double bond in the olefin. Attenuation of aluminum chloride with nitromethane prevents product isomerization even at the reflux temperature of benzene. Alkylation with both olefins in benzene solution in the presence of aluminum chloride–nitromethane results in widely different isomer distributions which approach each other if the alkylation reaction is carried out in nitromethane solution. These results are explained in terms of formation of secondary carbonium ions with relative stabilities and reactivities that are affected by the solvent and the mobility of the negative ion in the ion pair.

Alkylation of aromatic compounds with various alkylating agents in the presence of strong Friedel–Crafts catalysts such as aluminum chloride has long been known to be accompanied by isomerization and transalkylation.[1-5] This is especially important in the investigation of substrate selectivity and orientation of alkyl groups in di- and polyalkylation. The extent of this isomerization and disproportionation, which alters the product distribution, is determined by the severity of the reaction conditions, namely the strength and amount of the catalysts, the temperature, and the time of the reaction. The same question also occurs in the alkylation of benzene with long-chain α olefins where the products initially formed undergo extensive isomerization in the presence of excess aluminum chloride.[6,7] Thus, Nenitzescu has concluded that the Friedel–Crafts alkylation leading to the formation of phenylalkanes is a kinetically controlled reaction, but the subsequent isomerization of phenylalkanes is a thermodynamically controlled reaction leading to the most stable isomer, which is not always identical with the phenylalkane formed from the most stable carbonium ion.[8] The situation is also somewhat complicated by the fact that isomerization of the initial products can be shifted beyond thermodynamic equilibrium by an excess of $BF_3 \cdot HF$ or $AlCl_3 \cdot HCl$ which often results in the formation of only the product whose intermediate complex with the catalyst is the most stable one.[9] Therefore, it is of interest to find out if the phenylalkanes obtained from the alkylation of benzene with a long-chain α olefin such as 1-dodecene in the presence of aluminum chloride come to equilibrium as a result of their isomerization by the strong catalyst, and if this equilibrium distribution differs from the initial isomer distribution obtained in the absence of product isomerization. It is also of interest to find out if the intermediate carbonium ions also come to equilibrium before they attack benzene and if this equilibrium distribution differs from the final equilibrium distribution obtained as a result of isomerization of the products themselves.

Results

Since alkylation with aluminum chloride proceeds rapidly only after an incubation period during which the so-called red oil forms,[10] the reaction was run in the presence of a small amount (about 20% of the catalyst) of a catalyst layer from a previous alkylation of the same system. At 35° and using 0.12 mol of the catalyst/mol of the olefin, both 1-dodecene and *trans*-6-dodecene afforded nearly identical isomer distribu-

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