at 0°. A rapid increase in pressure was observed (Fig. 7). After 9.5 hours, the volatile material was removed and analyzed. There was obtained 1.29 mmoles (41% conversion) hydrogen bromide (v.p. 35.0 mm. at −112°) and 1.74 mmoles isopropyl bromide (v.p. 70.1 mm. at 0°, $n^{20}\mathrm{D}$ 1.4260). The hydrogen bromide and isopropyl bromide represent a 95% recovery of the bromine originally present in the alkyl halide. During the reaction the solution was red in color. During the removal of the products, the residue in the tube became much deeper red and very viscous. It possessed the appearance of a typical Friedel–Crafts "red oil."

A similar experiment was carried out using 1.154 mmoles of aluminum bromide in 4.87 mmoles of *n*-propyl bromide. The evolution of hydrogen bromide proceeded much as in the previous experiment (Fig. 7). (The higher pressures are approximately of the magnitude to be anticipated from the larger amount of catalyst present.) After 9 hours, the volatile materials were removed. There was obtained 1.92 mmoles (40% conversion) of hydrogen bromide and 2.70 mmoles of isopropyl bromide. No significant concentration of the original *n*-propyl bromide could be detected. Again the hydrogen bromide and isopropyl bromide represent a material recovery of 95%.

When *n*-propyl bromide and aluminum bromide were maintained at −80°, the solution was only slightly colored and there was little or no evolution of gas. After 11.7 hours, trimethylamine was added to deactivate the catalyst and permit recovery of the alkyl halide. The product, analyzed by refractive index, contained 27.6% isopropyl bromide. In another experiment, the isomerization contained hydrogen bromide. After 17.6 hours, the hydrogen bromide was removed, the aluminum bromide deactivated with trimethylamine, and the product recovered. In this experiment the product contained 38.3% isopropyl bromide. Considering the difference in reaction times it is apparent that the reaction rates were approximately the same in the two experiments.

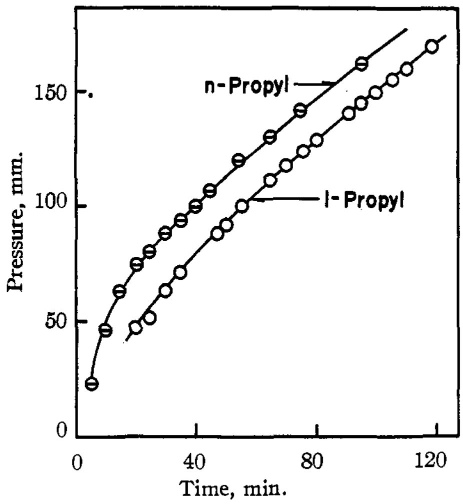

Fig. 7.—Pressure increase above solutions of aluminum bromide in the propyl bromides at 0°.

LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

# Kinetics of the Reaction of Representative Benzyl Halides with Aromatic Compounds; Evidence for a Displacement Mechanism in the Friedel–Crafts Reactions of Primary Halides[1,2]

BY HERBERT C. BROWN AND MARTIN GRAYSON[3]

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A kinetic study has been made of the reactions of several benzyl halides with various aromatic compounds under the catalytic influence of aluminum chloride in nitrobenzene solution. Both benzyl chloride and *p*-chlorobenzyl chloride react too rapidly for convenient measurement; therefore 3,4-dichloro- and *p*-nitrobenzyl chlorides, which react at more convenient rates, were primarily utilized in the kinetic studies. The rate data reveal that the reaction is third order—first order in aromatic component, first order in aluminum chloride ($AlCl_3$), and first order in the benzyl halides. The rate increases with increasing basic properties of the aromatic component: $ClC_6H_5 < C_6H_6 < CH_3C_6H_5 < m\text{-}(CH_3)_2C_6H_4$. Slower, competitive dialkylation reactions were observed at low aromatic concentrations. The kinetic analysis of the consecutive reactions was confirmed by the preparation of 3,4-dichlorodiphenylmethane and measurement of its rate of reaction with 3,4-dichlorobenzyl chloride. The reaction is not very sensitive to the dielectric constant of the solvent. A displacement mechanism involving nucleophilic attack by the aromatic component on an alkyl halide–aluminum chloride addition compound is consistent with the observations. Moreover, this mechanism offers a simple, reasonable explanation for the observed formation of *n*-propylbenzene in the Friedel–Crafts alkylation of benzene with either *n*-propyl halides or alcohol.

## Introduction

The mechanism which is generally accepted at the present time for the Friedel–Crafts reaction involves ionization of the alkyl halide under the influence of the catalyst, followed by the electrophilic substitution of the aromatic nucleus by the carbonium ion.[4]

$$RX + MX_3 \rightleftarrows R^+ + MX_4^-$$
$$ArH + R^+ \longrightarrow ArR + H^+$$
$$H^+ + MX_4^- \longrightarrow HX + MX_3$$

This theory is supported primarily by observations that the reaction is enhanced by strong electrophilic catalysts and easily ionized alkyl halides[4] and rearrangements characteristic of carbonium ions are common during alkylation.[5]

This ionization mechanism, however, does not account for the high yields of *n*-propylbenzene obtained in the alkylation of benzene with *n*-propyl chloride[6] and the sole formation of the *n*-propyl isomer in the alkylation of benzene with *n*-propyl alcohol and aluminum chloride.[6] Moreover, the same workers also report that neopentylbenzene is formed in the alkylation of benzene with neopentyl alcohol and aluminum chloride.[7] These observations suggest a displacement mechanism.

[1] The Catalytic Halides. IX.

[2] Based upon a thesis submitted by Martin Grayson in partial fulfillment of the requirements for the Ph.D. degree.

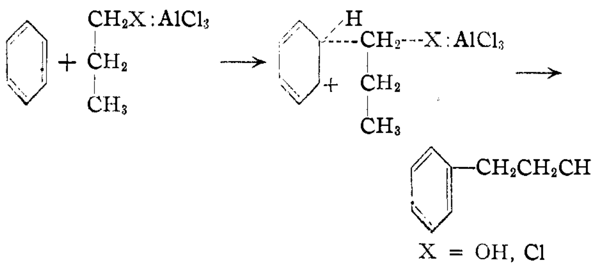
[3] Standard Oil Company (Indiana) Fellow, 1949–1950; A.E.C. Fellow, 1950–1952.

[4] C. C. Price, *Chem. Revs.*, **29**, 37 (1941); "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., pp. 1–82.

[5] D. V. Nightingale, *ibid.*, **25**, 329 (1939).

[6] V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

[7] H. Pines, L. Schmerling and V. N. Ipatieff, THIS JOURNAL, **62**, 2901 (1940).



X = OH, Cl

A detailed study of the kinetics of aromatic alkylation by primary halides offered promise as a suitable test for the existence of such a displacement mechanism. It was previously shown by Bartlett and his co-workers[8] that the exchange reaction of *t*-butyl bromide and isopentane under the influence of aluminum bromide, a reaction that is believed to proceed through the formation of the *t*-butylcarbonium ion, is over in less than 0.002 sec. at 25°.

$$(CH_3)_3CBr + {}^1/_2Al_2Br_6 \rightleftarrows (CH_3)_3C^+ + AlBr_4^-$$

$$(CH_3)_3C^+ + HC(CH_3)_2C_2H_5 \rightleftarrows (CH_3)_3CH + {}^+C(CH_3)_2C_2H_5$$

Moreover, Condon and Matuszak[9] have shown that the reaction of the isopropylcarbonium ion with benzene is some 350 times faster than the above reaction of the ion with a tertiary aliphatic hydrocarbon. It follows that the reaction of a simple alkyl carbonium ion with an aromatic hydrocarbon, the second step of the proposed mechanism for aromatic alkylation,[4] must be a very fast reaction. Since Friedel–Crafts reactions can be made to proceed at moderate, measurable rates, it must be concluded that the first step of the reaction must represent the slow, rate-determining stage. If so, the rate of aromatic alkylation should be determined solely by the rate of ionization of the alkyl halide and should be independent of the concentration or nucleophilic characteristics of the aromatic constituent undergoing alkylation.

On the other hand, if the reaction involves a displacement reaction, then the rate should depend both on the concentration and the nucleophilic character of the aromatic present.

Unfortunately, in spite of the immense quantity of literature dealing with the Friedel–Crafts reaction, there is not now available a single kinetic study in which the order of the reaction has been established with regard to the aromatic component. The majority of the investigations involve heterogeneous systems or make use of unsatisfactory analytical methods.[10] Ulich and Heyne[10] recognized the need for a homogeneous system and examined the reaction of *n*-propyl chloride with benzene in carbon disulfide solution, using gallium trichloride as the catalyst. Unfortunately, the authors failed to recognize the complexity of the system. They followed the reaction by the rate of evolution of hydrogen chloride, but did not establish that the rate of evolution of the gas corresponded to the rate of aromatic alkylation. In the similar *n*-propyl bromide–aluminum bromide system we have observed both isomerization of the *n*-propyl bromide to isopropyl bromide and rapid hydrogen bromide evolution at 0° in the absence of aromatic hydrocarbon.[11] Furthermore, in the presence of aromatic hydrocarbons and gallium trichloride, hydrogen chloride is absorbed, presumably to form $\sigma$-complexes.[12] Before the kinetics of the reaction of *n*-propyl halides with aromatic hydrocarbons can be fully understood, it will be necessary to establish the significance of these factors in the over-all reaction.

The kinetic study by Olivier and Berger[13] is free of these objections. These authors utilized the reaction of aromatic hydrocarbons with the isomeric nitrobenzyl halides, and followed the rate of reaction by isolation and analysis of the unreacted benzyl halide. The reactions were carried out at 30° in excess of the aromatic component as the solvent, using a 1:1 addition compound of aluminum chloride and the nitrobenzyl halide ($AlCl_3 \cdot O_2NC_6H_4CH_2Cl$) as the reactant. They report first-order rate constants for the reaction with *p*-nitrobenzyl chloride: 0.00084 $min.^{-1}$ for chlorobenzene, 0.0045 for benzene and 0.0105 for toluene.

The dependence of the rate constant on the structure of the aromatic suggests that the aromatic is indeed participating in a nucleophilic displacement in the rate-determining step. Unfortunately, the aromatic component was used as the solvent and one cannot, therefore, exclude the possibility that the observed differences in rates may arise from solvent effects. To obtain definite evidence as to the participation of the aromatic component in the rate-determining step of Friedel–Crafts reactions of primary halides, we decided to extend Olivier and Berger's observations under conditions which would permit independent variation of the concentration of the benzyl halide, aromatic, and catalyst.

Accordingly, we carried out a kinetic investigation of the reaction of substituted benzyl halides in nitrobenzene solution with several aromatic compounds. Aluminum chloride dissolved in the solvent was used as the catalyst. The reaction was followed by analysis for the increase in hydrochloric acid with time after correcting for that formed by hydrolysis of the aluminum chloride used as catalyst. The results definitely establish that the aromatic component is involved in the rate-determining stage of the reaction.

## Results and Discussion

Benzyl chloride and *p*-chlorobenzyl chloride were observed to react with benzene too rapidly for convenient measurement. Moreover, the reaction of benzene with *p*-nitrobenzyl chloride in dilute nitro-

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[8] P. D. Bartlett, F. E. Condon and A. Schneider, This Journal, **66**, 1531 (1944).

[9] F. E. Condon and M. P. Matuszak, *ibid.*, **70**, 2539 (1948).

[10] (a) D. B. Steele, *J. Chem. Soc.*, **83**, 1470 (1903); (b) L. F. Martin, P. Pizzolato and L. S. McWaters, This Journal, **57**, 2584 (1935); (c) H. Clement, *Ann. chim.*, **13**, 243 (1940); (d) H. Ulich and G. Heyne, *Z. Elektrochem.*, **41**, 509 (1935).

[11] H. C. Brown and W. J. Wallace, This Journal, **75**, 6279 (1953).

[12] Unpublished work with L. P. Eddy. For previous work on the formation of these complexes see D. A. McCaulay and A. P. Lien, This Journal, **73**, 2013 (1951); H. C. Brown and H. W. Pearsall, *ibid.*, **74**, 191 (1952); H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6268 (1953).

[13] S. C. J. Olivier and G. Berger, *Rec. trav. chim.*, **45**, 710 (1926).

benzene solution at 25° was somewhat slow. However, the reaction involving 3,4-dichlorobenzyl chloride proceeded at a convenient rate under these conditions and this halide was therefore employed for a detailed study of the reaction kinetics.

**The Reaction of 3,4-Dichlorobenzyl Chloride with Benzene.**—Study of the kinetics of the reaction of 3,4-dichlorobenzyl chloride with benzene clearly revealed that the reaction is first order in the benzyl halide and in the aluminum chloride (Table I). Thus, in kinetic studies 1–3 a tenfold variation in the concentration of the 3,4-dichlorobenzyl chloride did not result in any change in the calculated first-order rate constant. Similarly, within the experimental error, the calculated first-order rate constants varied linearly with the initial aluminum chloride concentration (kinetic studies 4 and 5, Table I).

TABLE I

SUMMARY OF RATE DATA FOR THE REACTION OF BENZENE WITH 3,4-DICHLOROBENZYL CHLORIDE AND ALUMINUM CHLORIDE IN NITROBENZENE SOLUTION AT 25°

| Kinetic study | Concentration (moles/l.) $C_6H_6$ | RCl | $AlCl_3$ | First-order constant $k_1$(hr.$^{-1}$) | Second-order constant $k_2$(l. mole$^{-1}$ hr.$^{-1}$) |
|---|---|---|---|---|---|
| 1 | 0.335 | 0.333 | 0.333 | 0.96 ± 0.07 | |
| 2 | .335 | 1.00 | .333 | 0.94 ± .03 | |
| 3 | .335 | .111 | .333 | 1.04 ± .17[a] | |
| 4 | .335 | .333 | .111 | 0.30 ± .02 | |
| 5 | .335 | .333 | .667 | 1.64 ± .07[b] | |
| 6 | 1.00 | .333 | .333 | 1.95 ± .07 | 2.13 ± 0.06 |
| 7 | 0.500 | .333 | .333 | 1.07 ± .09 | 2.07 ± .08 |
| 8 | 1.67 | .333 | .333 | 2.59 ± .09 | 1.68 ± .08 |

[a] Low precision due to small quantities of hydrogen chloride formed. The hydrogen chloride was determined by a differential titration (see Experimental Part). [b] The solution was very viscous and difficulty was encountered in making a complete transfer of the solution from the pipet to the reaction capsule.

The order with regard to benzene offered a more difficult problem. The excellent first-order constants which could be calculated from the expression

$$d[HCl]/dt = k_1[RCl]$$

in runs 1–5 suggested that the reaction was indeed independent of the benzene concentration. However, a threefold increase in the benzene concentration resulted in a twofold increase in the calculated first-order rate constant (run 6), while a fivefold increase resulted in a relatively minor further increase in $k_1$ (run 8). Attempts to calculate a second-order rate constant were unsuccessful.

In one experiment the initial benzyl halide concentration was made greater than the initial benzene concentration. Hydrogen chloride was formed in amounts much greater than would correspond to the initial benzene concentration and the calculated value of the first order rate constant showed only a gradual decline with time. Under the same conditions but in the absence of the aromatic component the solutions are stable and do not form hydrogen chloride. It was, therefore, concluded that the kinetic data were being complicated by one or more consecutive reactions involving the further alkylation of the initial product at rates comparable to that of the initial reaction

$$RCl + C_6H_6 + AlCl_3 \xrightarrow{k_1'} RC_6H_5 + HCl + AlCl_3$$

$$RCl + RC_6H_5 + AlCl_3 \xrightarrow{k_1''} R_2C_6H_4 + HCl + AlCl_3$$

Under these conditions ($k_1' \approx k_1$) the total concentration of the reactive aromatic ($C_6H_6 + RC_6H_5 + \ldots$) does not change with time and the over-all process must follow first-order kinetics. Only if $k_1'$ and $k_1''$ differed significantly would the reaction deviate from strict first-order kinetics. In the presence of relatively high initial concentrations of the aromatic, on the other hand, polyalkylation should become small and negligible and permit calculation of a second order constant which includes the change of benzene concentration with time. The values of $k_2$ calculated in this way for solutions 0.5 *M* in benzene (run 6) and 1.0 *M* in benzene (run 7) agree satisfactorily. With a still higher concentration of benzene, 1.67 *M*, the value of $k_2$ drops slightly (run 8). This decrease is presumably a result of the dilution of the solvent which in this kinetic study contained 17% benzene by volume. We observed similar decreases when the nitrobenzene was diluted with inert hydrocarbons. Similar data were obtained in the reactions of chlorobenzene and *m*-xylene with 3,4-dichlorobenzyl and *p*-nitrobenzyl chlorides. *It therefore appears safe to conclude that the reaction is first order in the aromatic component and the aromatic must therefore participate in the rate-determining stage.*

This interpretation of the experimental results was tested by a more detailed analysis of the kinetic data (run 1). Swain[14] has calculated a series of $k_1''/k_1'$ values for various $kt$ values at 15, 35 and 70% reaction for consecutive first-order processes involving the rate constants $k_1'$ and $k_1''$. Since our data (run 1) were well expressed in terms of a pseudo first-order constant, we could utilize Swain's treatment. A plot of $a-x$ *vs.* time was prepared and $t$ was estimated as 0.17, 0.46 and 1.23 hours at 15, 35 and 70% reaction, respectively. The results are given in Table II.

TABLE II

CALCULATION OF THE SPECIFIC RATES OF MONO- AND DIALKYLATION FOR THE REACTION OF BENZENE WITH 3,4-DICHLOROBENZYL CHLORIDE

| | Assumed first-order rate constant, $k_1$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Reaction, % | 0.98 | | 2.12 | | 1.70 | | 1.90 | |
| | $k_1't$ | $k_1''/k_1'$ | $k_1't$ | $k_1''/k_1'$ | $k_1't$ | $k_1''/k_1'$ | $k_1't$ | $k_1''/k_1'$ |
| 15 | 0.167 | 100 | 0.360 | 0.01 | 0.289 | 1.5 | 0.323 | 0.50 |
| 35 | .45 | 32 | .975 | .25 | .78 | .82 | .874 | .48 |
| 70 | .125 | 13 | 2.71 | .44 | 2.18 | .66 | 2.43 | .50 |

From this treatment it appears that $k_1'$ is 1.90 hr.$^{-1}$ for monoalkylation and $k_1''$ is 0.95 hr.$^{-1}$ for the dialkylation reaction. The direct determination of $k_1$ under conditions where polyalkylation must be negligible (Table I, run 6), resulted in a value of 1.95 hr.$^{-1}$. If this value is accepted for $k_1'$, then $k_1''$ becomes 0.98 hr.$^{-1}$. To test this, we prepared the monoalkylation product, 3,4-dichlorodiphenylmethane, and determined the rate of its reaction with 3,4-dichlorobenzyl chloride under conditions conducive to the monoalkylation reaction (initial concentration of the aromatic 1.0 *M*). The ob-

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[14] C. G. Swain, THIS JOURNAL, 66, 1696 (1944).

served value for $k_1''$, 1.07 ± 0.08 hr.$^{-1}$ constitutes a satisfactory check of the calculated value 0.98 hr.$^{-1}$.

The validity of this analysis is supported by another approach. We can represent the complete kinetic expression as

$$\frac{d[HCl]}{dt} = k_1'[RCl][C_6H_6] + k_1''[RCl][RC_6H_5] + \ldots..$$

where $k_1' = k_3[AlCl_3]$, $k_1'' = k_3[AlCl_3]$, etc. Ignoring terms past that corresponding to the dialkylation stage, this expression reduces to

$$\frac{d[HCl]}{dt} = [RCl]\,(k_1'[C_6H_6] + k_1''[RC_6H_5])$$

Since the total concentration of the reactive aromatic component is essentially constant, this equation reduces to the expression

$$\frac{d[HCl]}{dt} = K[RCl]$$

where

$$K = k_1'[C_6H_6] + k_1''[RC_6H_5]$$

If we neglect $R_2C_6H_4$ and higher polyalkyl products, the value of $[C_6H_6] + [RC_6H_5]$ becomes 0.33 *M*, equal to the initial concentration of benzene. If $k_1'$ and $k_1''$ do not differ greatly, we can write the approximate relationship

$$K \approx 0.33\,(1.95 + 1.07)$$
$$\approx 1.01 \text{ hr.}^{-1}$$

The observed value (Table I, run 1) was 0.96 ± 0.07 hr.$^{-1}$.

In view of the internal agreement between these different approaches, it appears certain that this reaction follows third-order kinetics with the rate being first order in the aromatic, the benzyl halide and aluminum chloride

$$\frac{d[HCl]}{dt} = k_3[AlCl_3][RCl][C_6H_6]$$

The rate of the reaction also was determined at 15° ($k_1$ = 0.239 ± 0.013 hr.$^{-1}$) and 35° ($k_1$ = 2.20 ± 0.14 hr.$^{-1}$). At each of these temperatures the ratio of $k_1''/k_1'$ was calculated and found to be 0.5, just as at 25°. Evidently the ratio of the consecutive rate constants does not change rapidly with temperature. These rate data yield an energy of activation of 19.6 kcal./mole with log PZ = 14.3.

**The Reaction of 3,4-Dichlorobenzyl Chloride with Other Aromatics.**—In the same manner the reactions of 3,4-dichlorobenzyl chloride with chlorobenzene, toluene and *m*-xylene were examined. The results are given in Table III.

TABLE III

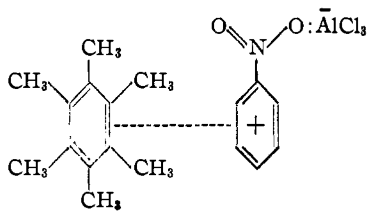
RATE CONSTANTS FOR THE REACTION OF 3,4-DICHLOROBENZYL CHLORIDE WITH AROMATICS IN NITROBENZENE SOLUTION AT 25°

| Aromatic | Third-order constant $k_3$(l.$^2$ mole$^{-2}$ sec.$^{-1}$) × $10^3$ | Relative rates |
|---|---|---|
| Chlorobenzene | 0.745 ± 0.020 | 0.47 |
| Benzene | 1.58 ± .05 | 1.00 |
| Toluene | 2.60 ± .08 | 1.64 |
| *m*-Xylene | 3.30 ± .10 | 2.08 |

Several attempts were made to obtain rate data for the reaction of mesitylene and naphthalene with 3,4-dichlorobenzyl chloride. In the case of mesitylene the reaction mixture was bright red, in contrast to the only weakly colored solutions obtained with the other substances. Naphthalene gave a deep red solution which darkened and became almost black and quite opaque. In neither case was it possible to obtain definitely end-points in the titrations. In view of the colors, it was considered that the difficulties might arise from complex formation in solution. It was observed that a reaction mixture which was 0.167 *M* in hexamethylbenzene and 0.332 *M* in aluminum chloride was dark red in color and gave indistinct end-points.

In order to compare the relative magnitudes of the interaction of various aromatic hydrocarbons with aluminum chloride in nitrobenzene, we prepared a series of solutions, 0.5 *M* in aluminum chloride and in aromatic hydrocarbon. The following colors were observed: no hydrocarbon, light yellow; benzene, light yellow; toluene, yellow orange; *m*-xylene, light orange; mesitylene, bright red; naphthalene, deep red becoming black; hexamethylbenzene, deep red.

In another experiment a dilute solution of nitrobenzene and aluminum chloride in carbon disulfide was prepared and small quantities of hexamethylbenzene in nitrobenzene were added. The color intensity increased until the ratio of hexamethylbenzene to aluminum chloride was 1:1 and then remained constant with increasing amounts of the hydrocarbon. These results indicate that there is stable ternary complex formation involving the three components in 1:1:1 composition. It would appear that the aluminum chloride greatly increases the electrophilic character of the nitrobenzene molecule and brings about stable complex formation with aromatic hydrocarbons of high basicity.



It is well known that the acylation of naphthalene in carbon disulfide gives a ratio of α- to β-substitution of 3:1 whereas acylation in nitrobenzene gives 90% of the β-ketone.[15] No entirely satisfactory mechanism has been proposed. It may be that the reaction in nitrobenzene involves acylation of the aluminum chloride–nitrobenzene–naphthalene complex. In such a complex the electron distribution in the hydrocarbon could be quite different from that in the free compound and result in an altered orientation.

**Alkylations with *p*-Nitrobenzyl Chloride.**—The reaction of *p*-nitrobenzyl halide with benzene and with *m*-xylene in nitrobenzene solution also exhibits third-order kinetics. At 25° the rate constant for the benzene reaction is 4.78 × $10^{-6}$ (l.$^2$ mole$^{-2}$ sec.$^{-1}$), while the corresponding rate con-

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[15] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 765. See also G. Baddeley [*J. Chem. Soc.*, 599 (1949)] for a careful study of this reaction.

stant for *m*-xylene is $23.8 \times 10^{-6}$. The two rate constants differ by a factor of 4.98 as compared to the factor 2.08 observed in the case of the corresponding reactions involving 3,4-dichlorobenzyl chloride.

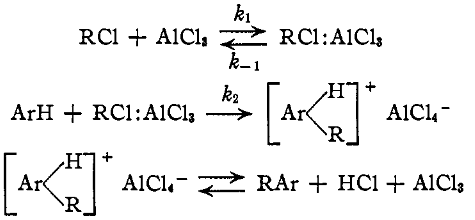
**The Effect of Solvent upon the Rate.**—The reaction of 3,4-dichlorobenzyl chloride with benzene was carried out in nitrobenzene solutions containing 10, 40 and 60% methylcyclohexane as diluent. Solutions containing higher concentrations of the hydrocarbon could not be used—separation into two phases occurred.

The following first-order rate constants (hr.$^{-1}$) were observed: 0% methylcyclohexane, $0.96 \pm 0.07$; 10%, $0.91 \pm 0.08$; 40%, $0.62 \pm 0.04$; 60%, $0.48 \pm 0.02$.

We also examined the rate of reaction of *p*-nitrobenzyl chloride with benzene at 25° in nitrobenzene solution containing 50 and 83% benzene by volume. Values of $k_3$ of $0.24 \times 10^{-5}$ and $0.19 \times 10^{-5}$ were obtained as compared to $0.478 \times 10^{-5}$ for essentially 100% nitrobenzene solutions. It follows that here also there appears to be only a small decrease in rate with increasing hydrocarbon content of the solvent.[16]

**The Reaction Mechanism.**—The results appear to eliminate the simple ionization mechanism for the reaction under consideration. Rate determining ionization of the benzyl halide followed by rapid attack on the aromatic reactant by the carbonium ion is excluded by the dependence of the reaction rate on the structure and concentration of the aromatic reactant. Similarly, a mechanism involving rapid ionization of the benzyl halide followed by rate determining electrophilic displacement is not acceptable since the *p*-nitrocarbonium ion, a more reactive entity than the benzyl carbonium ion, should then react more rapidly with the aromatics. Only if the rates of both stages of the reactions are comparable, is it possible to entertain an ionization mechanism. However, reactions which proceed by an ionization stage are powerfully affected by changes in the dielectric constant or ionizing properties of the medium. For example a change from 100% ethanol to 50% aqueous ethanol changes the rate of hydrolysis of *t*-butyl chloride from $9.70 \times 10^{-8}$ to $3.67 \times 10^{-4}$, a factor of approximately 30,000.[17] In the present case a change from essentially 100% nitrobenzene to 40% nitrobenzene–60% methylcyclohexane resulted in a change in the rate only by a factor of 2. This relatively small effect of the dielectric constant of the medium on the reaction rate is characteristic of bimolecular displacement mechanisms. For example in the reaction of triethylamine with benzyl bromide[18] at 21° the ratio of rates in 100% nitrobenzene and in 50% nitrobenzene–50% benzene is 171.7/61.6 or 2.8.

We believe that the experimental facts are more consistent with a mechanism involving a rate-determining nucleophilic attack by the aromatic component on a polar benzyl halide–aluminum chloride addition compound.

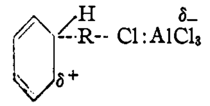


$$\mathrm{RCl} + \mathrm{AlCl_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCl{:}AlCl_3}$$

$$\mathrm{ArH} + \mathrm{RCl{:}AlCl_3} \xrightarrow{k_2} \left[\mathrm{Ar}{<}{}^{\mathrm{H}}_{\mathrm{R}}\right]^+ \mathrm{AlCl_4^-}$$

$$\left[\mathrm{Ar}{<}{}^{\mathrm{H}}_{\mathrm{R}}\right]^+ \mathrm{AlCl_4^-} \rightleftharpoons \mathrm{RAr} + \mathrm{HCl} + \mathrm{AlCl_3}$$

The transition state in the displacement step would then be represented as a σ-complex containing a partially formed carbon–carbon bond and a partially broken carbon–chlorine bond.



In this mechanism the first step should actually be written as an exchange between the nitrobenzene–aluminum chloride complex and the benzyl halide

$$\mathrm{RCl} + \mathrm{C_6H_5NO_2{:}AlCl_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCl{:}AlCl_3} + \mathrm{C_6H_5NO_2}$$

However, since nitrobenzene is the solvent, it is not necessary to include it in the rate expression. It should be pointed out that stable 1:1 complexes of the type postulated here for the benzyl halides have been isolated in the case of methyl chloride–gallium chloride,[19] $\mathrm{CH_3Cl{:}GaCl_3}$ and methyl bromide–aluminum bromide,[11] $\mathrm{CH_3Br{:}AlBr_3}$.

For the proposed mechanism we can write the complete rate expression

$$v = \frac{k_1 k_2 [\mathrm{AlCl_3}][\mathrm{RCl}][\mathrm{ArH}]}{k_{-1} + k_2[\mathrm{ArH}]}$$

When $k_{-1}$ is very large compared to $k_2$ (the equilibrium concentration of $\mathrm{RCl{:}AlCl_3}$ must be small since nitrobenzene is a much stronger base than are alkyl halides), the expression reduces to the third order law

$$\begin{aligned} v &= k_1 k_2 [\mathrm{AlCl_3}][\mathrm{RCl}][\mathrm{ArH}]/k_{-1} \\ &= k_3 [\mathrm{AlCl_3}][\mathrm{RCl}][\mathrm{ArH}] \end{aligned}$$

It will be observed that the third-order rate constant includes the term $k_1/k_{-1}$, the equilibrium constant for the formation of the $\mathrm{RCl{:}AlCl_3}$ addition compound. This offers a reasonable explanation for the very great difference in reactivity of the various benzyl halides—the ratio of rates for the reaction of 3,4-dichlorobenzyl chloride to *p*-nitrobenzyl chloride is 331/1. We have recently completed several studies on the effect of substituents on the ability of pyridine bases to unite with a proton and the corresponding effect of the ability of these bases to react with boron trifluoride.[20] A

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[16] From the data reported by Olivier and Berger[13] for the corresponding reaction in pure benzene at 30°, a value of $k_3$ of $8.5 \times 10^{-5}$ l.$^2$ mole$^{-2}$ sec.$^{-1}$ may be calculated. This is considerably higher than our values and suggests that in the absence of nitrobenzene in the solvent to coördinate with the aluminum chloride the reaction may proceed at a much faster rate. Unfortunately, our experimental techniques for handling the aluminum chloride could not be utilized in experiments designed to check this point and it was necessary to defer investigation of this question.

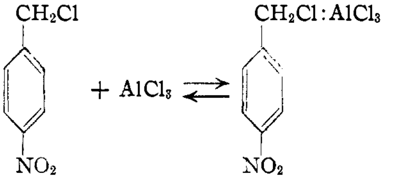
[17] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

[18] G. E. Mukhin, R. B. Ginzburg and K. M. Moiseeva, *Ukrainskii Khem. Zhur.*, **2**, 136 (1926); *C. A.*, **22**, 1264 (1928).

[19] H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953).

[20] Unpublished work with F. X. Mihm and R. M. Horowitz.

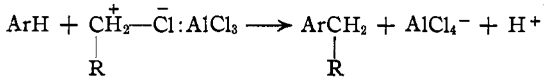
close correlation is observed. We may, therefore, anticipate that the basic properties of *p*-nitrobenzyl chloride, as evidenced by the equilibrium constant for the addition of aluminum chloride to the chlorine atom will be much less than for the corresponding reaction with 3,4-dichlorobenzyl chloride.



$(NO_2C_6H_4CH_2Cl < 3,4\text{-}Cl_2C_6H_3CH_2Cl < p\text{-}ClC_6H_4CH_2Cl < C_6H_5CH_2Cl)$

In an attempt to obtain a rough estimate of the magnitude of this effect we have utilized published data on the base strengths of the benzylamines[21] and Hammett's sigma values[22] to calculate values of $5.5 \times 10^{-6}$ and $7.6 \times 10^{-6}$ for $k_B$ for the *p*-nitro- and 3,4-dichlorobenzylamines, respectively.[23] Qualitatively, it is clear that the equilibrium constant ($k_1/k_{-1}$ in the rate expression) will be more favorable for 3,4-dichlorobenzyl chloride than for the *p*-nitro derivative. To account for the observed difference of 331 in the rate constants entirely in terms of the relative magnitudes of $k_1/k_{-1}$ would require a rho value for the reaction of $-14.15$.

If we use the revised $\sigma$-values recently proposed for electrophilic reactions[24] (*p*-$NO_2$ 0.778; *p*-Cl 0.10; *m*-Cl (est.) 0.164), we arrive at a rho value of $-4.90$. This is a more reasonable value for rho and suggests that the displacement reaction of the aromatic is with a polar partially-ionized addition compound.



$$ArH + \underset{R}{\overset{+}{C}H_2}-\overset{-}{Cl}:AlCl_3 \longrightarrow \underset{R}{ArCH_2} + AlCl_4^- + H^+$$

The results are, therefore, quite consistent with the concerted termolecular mechanism proposed by Swain for the substitution reactions of alkyl halides.[25] A more precise evaluation of the relative importance of bond-making *vs.* bond-breaking in the transition state must await completion of additional studies on the effect of substituents on the reaction rate.

It is also noteworthy that the ratio of the rate constants for *m*-xylene and benzene is increased from 2.08 with 3,4-dichlorobenzyl chloride to 4.98 for *p*-nitrobenzyl chloride. This increase is attributed to the relatively strong bond in *p*-nitrobenzyl chloride which must require a greater contribution from the hydrocarbon component in the transition state. The $\sigma$-complex of *m*-xylene is highly stable, compared to that of benzene.[26] Therefore, *m*-xylene is relatively more effective in the displacement reaction with *p*-nitrobenzyl chloride than with the more reactive 3,4-dichlorobenzyl chloride.

Finally, it is apparent that this mechanism accounts for the formation of 40–60% *n*-propylbenzene in the alkylation of benzene with *n*-propyl halides.[6] Presumably the formation of 60–40% of the isopropyl derivative arises from the concurrent isomerization of the *n*-propyl halide. It is known that the isomerization occurs under the conditions required for the alkylation.[11] In the alkylation of benzene with *n*-propyl alcohol and benzene, the formation of only the normal alkyl derivative is reported.[6] It is probable that under the reaction conditions *n*-propyl alcohol is not isomerized into the isopropyl derivative as readily as the corresponding halide.

Summing up it appears that the known facts about Friedel–Crafts alkylations involving *primary* halides and alcohols are best interpreted in terms of the displacement mechanism discussed in this paper and not in terms of the commonly accepted carbonium ion mechanism. We do not wish to imply that this conclusion will hold for all types of halides. Indeed there are reasons for concluding that tertiary halides probably react through a carbonium ion mechanism with secondary halides reacting preferentially, but not exclusively, through an ionization mechanism.[27] If this interpretation is supported by further work, the situation would then be very similar to the more common substitution reactions of alkyl halides in which both ionization and displacement mechanisms play a role.[25,28] We hope to place our understanding of the situation on a firmer basis through continued kinetic investigations of the Friedel–Crafts reaction.

## Experimental Part

**Materials.**—Nitrobenzene of at least 99.5 mole % purity (freezing point curve) was prepared by distilling technical grade (du Pont) nitrobenzene through a column (b.p. 73–74° at 5–6 mm.) and storing it over calcium hydride. The aromatic compounds used in the rate studies were the purest grade products available commercially and were distilled through a column rated at 70 plates and dried over calcium hydride.

*p*-Nitrobenzyl chloride (Eastman Kodak Co.) was recrystallized from absolute ethanol, m.p. 72.5–73°. 3,4-Dichlorobenzyl chloride (Heyden Chem. Co.) was distilled in an all glass column, b.p. 116° at 10 mm., $n^{20}D$ 1.5772.

The purity of the aluminum chloride is a critical factor in obtaining reproducible rate data. The commercial catalyst powder was sublimed in a long, all-glass system at a pressure less than 1 mm. to obtain a pure white product which was analytically pure. This product was always handled and stored under dry nitrogen.

**Procedure for the Kinetic Measurements.**—Molar solutions in nitrobenzene of aluminum chloride, the benzyl chloride and the aromatic were prepared. A 1-ml. transfer pipet, calibrated with nitrobenzene at 25°, was used to transfer an aliquot of the hydrocarbon and benzyl halide solutions into thin-walled glass capsules. The capsules were stoppered and brought to temperature in the bath. An aliquot of the catalyst solution, maintained at the reaction temperature, was introduced into the capsule and it was immediately sealed. After the desired reaction time, the capsule was crushed in 50 ml. of carbon dioxide-free distilled

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(21) W. H. Carothers, C. F. Bickford and G. J. Hurwitz, THIS JOURNAL, **49**, 2908 (1927).

(22) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., p. 188.

(23) The value of the rho constant was $-0.816$ (method of last squares, error in the sigma terms only). Sigma values of $+0.779$ for *p*-nitro and $+0.600$ for 3,4-dichloro (0.277 for *p*-chloro + 0.373 for *m*-chloro) were used.

(24) D. E. Pearson, J. F. Baxter and J. L. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(25) C. G. Swain, THIS JOURNAL, **70**, 1125 (1948); C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2993 (1948); C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951).

(26) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(27) C. C. Price and M. Lund, *ibid.*, **62**, 2105 (1940); R. L. Burwell and S. Archer, *ibid.*, **64**, 1032 (1942); R. L. Burwell, L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952).

(28) E. D. Hughes, *J. Chem. Soc.*, 968 (1946).

water (0°), the long stem of the capsule was washed and discarded. About 3 ml. of 0.5 $N$ barium hydroxide was added to neutralize excess acid, 30 ml. of 30% by weight potassium sodium tartrate solution introduced, and the titration carried to the end-point, using phenolphthalein as the indicator.[29] A blank determination on the catalyst solution gave the base required by the aluminum chloride. The hydrogen chloride produced in the reaction was obtained by difference.

**Reproducibility and Errors.**—No production of free acid from hydrolysis was observed in experiments in which the benzyl halide was maintained in contact with the solution utilized for the titration. Moreover, it was demonstrated that in the absence of aromatic only negligible amounts of free acid were produced by 3,4-dichlorobenzyl chloride and the catalyst. Finally, in the absence of the catalyst, solutions of the benzyl halide and the aromatic hydrocarbon were stable indefinitely.

Typical kinetic runs with 3,4-dichlorobenzyl chloride and *p*-nitrobenzyl chloride are reported in Tables IV and V. Experimental data for 3,4-dichlorobenzyl chloride are represented graphically in Figs. 1 and 2.

TABLE IV

RATE DATA[a] FOR THE REACTION OF BENZENE WITH 3,4-DICHLOROBENZYL CHLORIDE AT 25°

| Time, hr. | RCl reacted, % | Moles reacted, $x$ | Rate constant[b, c] $k_1$(hr.$^{-1}$) | $k_2$ (l. mole$^{-1}$ hr.$^{-1}$) |
|---|---|---|---|---|
| 0.10 | 18 | 0.0588 | 1.92 | 2.00 |
| .133 | 24 | .0806 | 2.08 | 2.17 |
| .20 | 34 | .114 | 2.09 | 2.24 |
| .25 | 39 | .129 | 1.97 | 2.12 |
| .30 | 44 | .148 | 1.95 | 2.13 |
| .50 | 60 | .200 | 1.83 | 2.08 |
| .75 | 75 | .250 | 1.84 | 2.20 |
| 1.00 | 85 | .286 | 1.94 | (2.41) |

[a] Initial concentrations: benzene, 1.00 $M$; 3,4-dichlorobenzyl chloride, 0.333 $M$; aluminum chloride ($AlCl_3$), 0.333 $M$. [b] For calculation of $k_1$, $a = 0.333$; for $k_2$, $a = 1.00$, $b = 0.333$. [c] Mean values: $k_1 = 1.95 \pm 0.07$ hr.$^{-1}$; $k_2 = 2.13 \pm 0.06$ l. mole$^{-1}$ hr.$^{-1}$.

TABLE V

RATE DATA[a] FOR THE REACTION OF BENZENE WITH *p*-NITROBENZYL CHLORIDE AT 25°

| Time, hr. | RCl reacted, % | Moles reacted, $x$ | Rate constant[b] $k_1$(hr.$^{-1}$) |
|---|---|---|---|
| 48.0 | 25 | 0.0833 | 0.00597 |
| 72.0 | 34 | .115 | .00583 |
| 96.0 | 41 | .137 | .00550 |
| 120.0 | 49 | .165 | .00567 |

[a] Initial concentrations: benzene, 1.00 $M$; *p*-nitrobenzyl chloride, 0.334 (= $a$); aluminum chloride ($AlCl_3$), 0.334. [b] Mean values: $k_1 = 0.00574 \pm 0.00016$ hr.$^{-1}$.

The runs in which the concentration of aromatic was smaller, comparable to the concentration of the benzyl halide, gave values for $k_1$ which tended to decrease with time. In view of the postulated complex nature of $k_1$, such a decrease would be anticipated. Unfortunately, the precision of the differential titration method made it impractical to attempt to determine the rate constant in the initial stages, below 20% reaction. The reproducibility of the procedure was checked by Mr. R. Lamb, utilizing independently prepared solutions. He obtained a value for $k_1$ of $1.57 \pm 0.05$ hr.$^{-1}$ for the reaction of toluene and 3,4-dichlorobenzyl chloride as compared to our value of $1.56 \pm 0.05$ hr.$^{-1}$ under the same conditions.

**3,4-Dichlorodiphenylmethane.**—The monoalkyl derivative, 3,4-dichlorodiphenylmethane was prepared in 64% yield from 400 g. (5.1 moles) of benzene, 2 g. of aluminum amalgam and 156 g. (0.80 mole) of 3,4-dichlorobenzyl chloride. The procedure was adapted from that for diphenylmethane.[30] The product was collected at 171–172° at 8 mm., $n^{20}D$ 1.5983. *Anal.* Calcd. for $C_{13}H_{10}Cl_2$: C, 65.84; H, 4.25; Cl, 29.91. Found: C, 65.85; H, 4.47; Cl, 30.06.

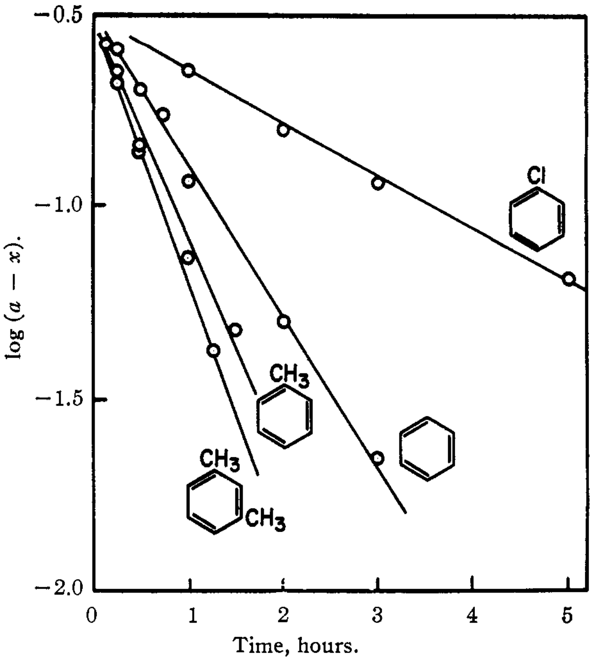

Fig. 1.—The rates of reaction of 3,4-dichlorobenzyl chloride with several aromatic hydrocarbons.

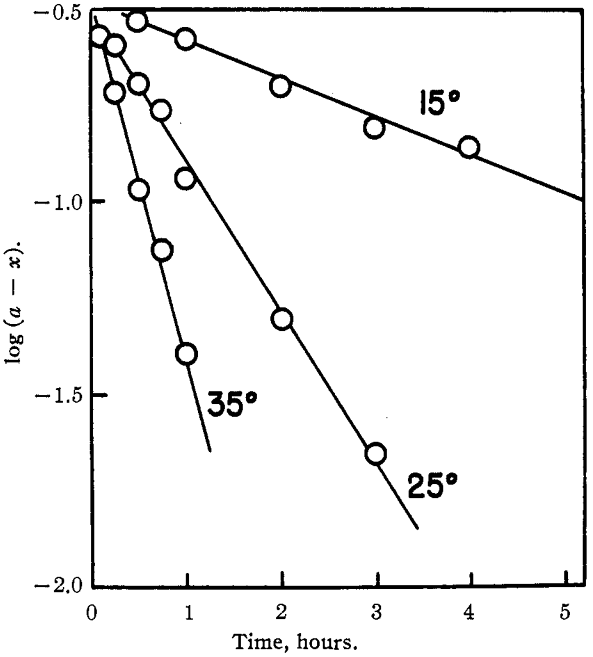

Fig. 2.—The rates of reaction of 3,4-dichlorobenzyl chloride with benzene at several temperatures.

A fore-run was obtained of 12.5 g. of material, b.p. 60–61° at 11 mm. and $n^{20}D$ 1.5508. It was identified as *o*-dichlorobenzene. Another fraction, b.p. 127–129° at 11 mm., $n^{20}D$ 1.5760, obtained in roughly equivalent yield, was identified as diphenylmethane. These substances presumably arise from

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[29] L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945).

[30] W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 232.

a transfer of a benzyl group from 3,4-dichlorodiphenylmethane to a benzene molecule.

$$C_6H_5CH_2C_6H_3Cl_2 + C_6H_6 \xrightarrow{HCl,\ AlCl_3} C_6H_5CH_2C_6H_5 + o\text{-}C_6H_4Cl_2$$

**The Hexamethylbenzene–Nitrobenzene–Aluminum Chloride Complex.**—A colorless solution of 0.01 mole of hexamethylbenzene (m.p. 160–162°) in carbon disulfide was mixed with a light yellow solution of 0.01 mole each of nitrobenzene and aluminum chloride in the same solvent. A dark red color developed immediately. The solvent was removed under reduced pressure. There was obtained a dark red-brown, almost black, crystalline solid. It reacted vigorously with water and was quite hygroscopic. It underwent gradual decomposition above 90–100°, but did not melt at temperatures above the m.p. of the 1:1 nitrobenzene–aluminum chloride complex. On hydrolysis, pure hexamethylbenzene could be recovered. Because of the characteristics of the material we did not attempt to prepare an analytical sample. The formation of a 1:1:1 complex was indicated by experiments on the variation of the color intensity as the composition was varied.

LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

# An Interpretation of Meta Orientation in the Alkylation of Toluene. The Relative Reactivity and Isomer Distribution in the Chloromethylation and Mercuration of Benzene and Toluene[1,2]

BY HERBERT C. BROWN AND K. LEROI NELSON[3]

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The high proportions of meta isomers observed in the alkylation of monoalkylbenzenes under "non-isomerizing" conditions are not anomalous. A detailed examination of the available data on isomer distribution in the substitutions of toluene clearly demonstrates that there is no sharp division between reactions which give a high proportion of meta substitution and those which give little or no meta substitution. We propose that the importance of meta substitution is related to the "activity" of the attacking species and utilize the relative reactivity of toluene and benzene in the reaction under consideration as a measure of this "activity." A plot of the log of the relative toluene/benzene reactivities *vs.* the log of the toluene para/meta ratios indicates a simple linear relationship. Although some discrepancies appear, the data in these cases are open to question. As a crucial test of our proposal we undertook a reinvestigation of the chloromethylation reaction. We found that no chloromethylation of benzene occurs under the conditions for which a toluene/benzene ratio of 3 is reported. For reaction with trioxymethylene and hydrogen chloride in the presence of zinc chloride in glacial acetic acid at 60°, we observed a toluene/benzene ratio of 112 ± 12 with the distribution of isomers from toluene being 34.7, 1.3 and 64.0% ortho, meta and para, respectively. These results are in excellent agreement with our proposal. From the existing data on the distribution of isomers from the mercuration of toluene at 25° we predicted a value of 15–20 for the toluene/benzene ratio. We found a value of 30 ± 3. The yield of meta isomer, 12.3%, was somewhat higher than that previously reported.

## Introduction

Orientations in Friedel–Crafts alkylations are frequently considered to be anomalous. Much of the early literature is confusing and misleading.[4,5] However, it is now definitely established that alkylation of aromatics with aluminum chloride and alkyl halides leads to the formation of considerable quantities of the *m*-dialkyl isomer.[6–8] Moreover, the exclusive formation of the meta isomer in the presence of molar quantities of the catalyst has been reported.[9] Although the possibility of forming larger yields of the meta isomer than those given by the thermodynamic equilibrium value has been questioned,[10] this result has been checked.[11] It was proposed[11] that the large yields of the meta isomer arise from isomerization[12] of the ortho and para derivatives to the more stable[13] σ-complexes[14] formed by the meta dialkylbenzenes.

This explanation nicely accounts for the high yields of meta isomer obtained under isomerizing conditions. It does not account for the formation of large amounts of the meta isomer under conditions where isomerization is not an important reaction. For example, Condon[8] has shown that no *o*- or *m*-cymene results when *p*-cymene is alkylated with propylene under mild conditions, yet under similar conditions all isomeric cymenes are obtained by the alkylation of toluene (Table I).

TABLE I

ISOMER DISTRIBUTION IN THE ISOPROPYLATION OF TOLUENE

| Temp., °C. | Catalyst | Isomer distribution Ortho | Meta | Para |
|---|---|---|---|---|
| 5 | $AlCl_3$–$MeNO_2$ or $BF_3$–$Et_2O$ | 37.5 | 29.8 | 32.7 |
| 65 | $AlCl_3$–$MeNO_2$ or $BF_3$–$Et_2O$ | 37.6 | 27.5 | 34.9 |

Numerous workers have proposed to account for the large yields of the meta isomer by "normal" alkylation to the 1,3,4-trialkyl derivative, followed by loss of the alkyl group in the 4-position.[4,5] Condon's results effectively rule out this explanation.

We propose that the high yield of the meta isomer

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[1] The Catalytic Halides. X.

[2] Based upon a thesis presented by K. LeRoi Nelson in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A.E.C. Fellow, 1950–1952.

[4] C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapt. I.

[5] A. W. Francis, *Chem. Revs.*, **43**, 257 (1948).

[6] K. T. Serijan, H. F. Hipsher and L. C. Gibbons, THIS JOURNAL, **71**, 873 (1949).

[7] J. H. Simons and H. Hart, *ibid.*, **69**, 979 (1947).

[8] F. E. Condon, *ibid.*, **71**, 3544 (1949).

[9] J. F. Norris and D. Rubinstein, *ibid.*, **61**, 1163 (1939).

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[11] D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

[12] G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

[13] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[14] H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).