Aromatic Substitution. XXX.[1] Friedel–Crafts Benzylation of Benzene and Toluene with Benzyl and Substituted Benzyl Halides

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Received August 28, 1971

Abstract: The Friedel–Crafts benzylation of benzene and toluene with benzyl and substituted benzyl chlorides has been investigated in the presence of various Lewis acid catalysts. Study of the $AlCl_3 \cdot CH_3NO_2$-catalyzed competitive benzylation of toluene and benzene, including variation of the reaction time, benzyl halide, aluminum halide, and solvent (nitromethane) concentration, and the nature of X in AlX_3 and $C_6H_5CH_2X$, leads to the conclusion that intermolecular selectivity (k_T/k_B) is very sensitive to the precise reaction conditions, *e.g.*, the nature of the benzyl cationic species, while intramolecular selectivity (isomer distribution) is less sensitive to conditions so far as unsubstituted benzyl halides are used. The effect of the nature of catalysts on the k_T/k_B value and isomer distribution was also examined by using a variety of Lewis acid catalysts. Friedel–Crafts catalysts were classified according to their activity in benzylations with methylbenzyl chlorides into four categories: A, very active catalysts which also bring about intra- and intermolecular isomerizations; B_1 and B_2, moderately active and weak catalysts, respectively, which bring about no isomerization; and C, very weak or inactive catalysts. The $TiCl_4$-catalyzed competitive benzylation of toluene and benzene with 16 substituted benzyl chlorides, in which all parameters are kept constant and only the electrophilicity of the reagent was changed systematically by substituents, showed a close relationship between electrophilicity and selectivity of the reagents. The results are interpreted by the indication that the transition state of highest energy is not a fixed one and can vary with ease from a late one resembling an intermediate (σ complex) to an early one resembling starting material (π complex). The observation of a good correlation between log k_T/k_B values and ^{13}C chemical shifts of benzyl cation centers further exemplifies that the nature of electrophiles plays the most important role in determining substrate selectivities. The kinetic study of benzylation of toluene and benzene as well as competitive rates proved that the k_T/k_B values from the competitive method and from the rate study (noncompetitive) are in excellent agreement within experimental error. Finally, the $TiCl_4$-catalyzed competitive benzylation of benzene with benzyl and substituted benzyl chlorides gives a linear relationship between log (k_R/k_H) and σ^+ for studied methyl, chloro, and fluoro substituents. Using relationships obtained in the present study, it was possible to derive ortho σ^+ values for these three substituent groups: $\sigma^+_{o\text{-CH}_3} = -0.19$, $\sigma^+_{o\text{-Cl}} = 0.33$, and $\sigma^+_{o\text{-F}} = 0.31$, respectively.

Electrophilic aromatic substitution is one of the most studied organic reactions.[3] A recent review by one of us[4] gave a summary of the general mechanistic considerations, as well as our own earlier work in the field.

In previous studies[5] we reported a series of electrophilic aromatic substitutions involving strongly electrophilic reagents, which showed low substrate selectivity in the form of low $k_{\text{toluene}}/k_{\text{benzene}}$ rate ratios, correlating well with π but not σ basicities of the aromatics,[4] but at the same high positional selectivity (generally high ortho:para isomer ratios with only a small amount of the meta isomer formed). We expressed our view that in these systems the transition state is of π and not of σ complex nature.

Our concepts attracted interest[3a] but were also criticized. In criticism[6] it was suggested that the above results could be a consequence of incomplete mixing before fast reaction with the very reactive electrophilic reagents.

Relating aromatic benzylation in an earlier publication with Kuhn and Flood, we reported[5c] that the aluminum chloride–nitromethane catalyzed Friedel–Crafts benzylation of aromatics with benzyl chloride gives rise to high positional but low substrate selectivity. To support this suggestion, Tsuge and Tashiro[7] reported that in competitive benzylation reactions using indium chloride as the catalyst, substrate selectivity was low, although somewhat different than in the benzylation reaction using $AlCl_3$–CH_3NO_2 as the catalyst,[8] while high positional selectivity was basically the same. They

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(1) (a) Part XXIX: G. A. Olah and S. Kobayashi, *J. Amer. Chem. Soc.*, **93**, 6964 (1971); (b) a preliminary communication appeared: G. A. Olah, M. Tashiro, and S. Kobayashi, *ibid.*, **92**, 6369 (1970).

(2) Postdoctoral Research Associates: (a) 1969–1971; (b) 1968–1969.

(3) (a) For current reviews see: R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1969; (b) L. Stock, "Aromatic Substitution Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1968; (c) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963); (d) G. A. Olah, "Friedel–Crafts and Related Reactions," Vol. I–IV, Wiley-Interscience, New York, N. Y., 1963–1964; (e) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," American Elsevier, New York, N. Y., 1965; (f) P. B. de La Mare and J. Ridd, "Aromatic Substitutions—Nitration and Halogenation," Academic Press, New York, N. Y., 1959; (g) E. Berliner, *Progr. Phys. Org. Chem.*, 2, 253 (1964); (h) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 264–417; (i) J. March, "Advanced Organic Chemistry, Reaction, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968 pp 376–441.

(4) G. A. Olah, *Accounts Chem. Res.*, 4, 240 (1971).

(5) (a) G. A. Olah, S. J. Kuhn, and S. Flood, *J. Amer. Chem. Soc.*, **83**, 4571 (1961); (b) G. A. Olah, S. J. Kuhn, S. Flood, and J. C. Evans, *ibid.*, **84**, 3687 (1962); (c) G. A. Olah, S. J. Kuhn, and S. Flood, *ibid.*, **84**, 1688 (1966); (d) G. A. Olah and N. Overchuk, *ibid.*, **87**, 5786 (1965).

(6) (a) C. D. Ritchie and H. Win, *J. Org. Chem.*, **29**, 3093 (1964); (b) W. S. Tolgyesi, *Can. J. Chem.*, **43**, 343 (1965) (for a rebuttal, see G. A. Olah and N. Overchuk, *ibid.*, **43**, 3279 (1965)); (c) J. D. Ridd, "Studies on Chemical Structure and Reactivity," Methuen, London, 1966, p 152; (d) H. C. Brown and R. A. Wirkkala, *J. Amer. Chem. Soc.*, **88**, 1453 (1966); (e) H. Cerfontain and A. Telder, *Recl. Trav. Chim. Pay-Bas.*, **86**, 377 (1967); (f) S. Y. Caille and R. J. P. Corriu, *Chem. Commun.*, 1251 (1967); *Tetrahedron*, **25**, 2005 (1969); and most notably (g) C. K. Ingold in "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 290.

(7) O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jap.*, 40, 125 (1967).

(8) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **84**, 1695 (1962).

also reported[7] that as a Friedel–Crafts benzylating agent, benzyl chloride–indium chloride has a higher activity than does *p*-chlorobenzyl chloride–indium chloride.

We undertook the present study to obtain more detailed information about the factors influencing substrate and positional selectivity in Friedel–Crafts benzylations and in general to gain a better understanding of the mechanism of electrophilic aromatic substitutions.

Results and Discussion

I. $AlCl_3$-CH_3NO_2-Catalyzed Benzylation of Toluene and Benzene with Benzyl Halides. Factors Influencing the Inter- and Intramolecular Selectivity. The method of competitive rate determination in a study of aromatic substrate selectivity is valid only if the observed relative rates are dependent on the concentrations and nature of the aromatic substrates. A further requirement is that side reactions (*i.e.*, transalkylation, disproportionation, and isomerization) do not occur in the reaction system.

In an earlier paper[5c] we reported, based on variation of the toluene:benzene mole ratio in competitive experiments, that there is indeed a first-order dependence on the aromatic substrate concentration in competitive benzylations. We also studied the effect of isomerization on the benzylation system.[9] We now undertook a detailed examination of all reaction conditions which may influence the substrate and positional selectivities in the competitive benzylation using $AlCl_3$-CH_3NO_2 as catalyst.

Effect of Reaction Time. Indication of Absence of Product Isomerization. Table I summarizes results of the study of reaction time at a reaction temperature of 50° on both the isomer distribution and the substrate selectivity. Data show that both are independent of the reaction time within a span of 1–10 min. These data strongly support the contention suggested in the previous work[9] that when the benzylation is carried out with $AlCl_3$-CH_3NO_2 as the catalyst, practically nonisomerizing conditions prevail. The complex, $AlCl_3$-CH_3NO_2, as characterized by Schmerling[10a] is an effective and quite soluble alkylation catalyst but considerably milder than $AlCl_3$.

Table I. The Effect of Reaction Time on the Competitive Benzylation of Benzene and Toluene with Benzyl Chloride-$AlCl_3$-CH_3NO_2 at 50° [a]

Time, min	k_T/k_B	—Methyldiphenylmethane, %— Ortho	Meta	Para
1	5.4	42.6	6.3	51.1
3	5.4	42.5	6.3	51.2
5	5.4	42.4	6.2	51.4
10	5.4	42.2	6.3	51.5

[a] Molar ratio of the reaction components: toluene:benzene:benzyl chloride:$AlCl_3$-CH_3NO_2 (20 wt/wt %) = 20:20:1:0.1.

It should be mentioned that in the $GaCl_3$-catalyzed benzylation of toluene and benzene with benzyl bromide, Brown and Bolto[10b] found very substantial dependence of isomer distribution with reaction times (as short as 0.01 sec) in excess aromatic hydrocarbons as solvent (see subsequent discussion).

Effect of the Concentration Ratio of the Reagents. In our earlier work[5c] k_T/k_B (intermolecular selectivity) for benzylation with benzyl chloride using $AlCl_3$-CH_3NO_2 catalyst was found to be ~3.5. In the present work (Table II) we found that the numerical value is somewhat dependent on concentrations of the reagents (particularly catalyst) and solvent systems.

Table II. The Effect of Catalyst Concentration on the Competitive $AlCl_3$-CH_3NO_2-Catalyzed Benzylation of Benzene and Toluene with Benzyl Chloride at 50° for 5 Min[a]

Cat: $C_6H_5CH_2Cl$	k_T/k_B	—Methyldiphenylmethane, %— Ortho	Meta	Para
0.05	5.9	42.1	6.2	51.7
0.10	5.4	42.4	6.2	51.4
0.15	5.3	41.5	5.8	52.7
0.20	5.1	42.7	6.3	51.1
0.25	4.9	41.8	5.9	52.4
0.30	4.9	42.2	6.1	51.7
1.0	4.5	42.6	6.0	51.4
(1.0)[b]	(3.2)	(43.5)	(4.5)	(52.0)
3.0	4.0	41.9	6.1	52.0
5.0	3.6	42.1	6.3	51.6
10.0	3.0	42.5	6.1	51.4

[a] Molar ratio of the reactants toluene:benzene:benzyl chloride:$AlCl_3$-CH_3NO_2 (20 wt/wt %) was 20:20:1.0:0.05-10.0. [b] From a previous study: G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **84**, 1688 (1962), in nitromethane solution at 25°.

In Table II it can be seen that increasing the ratio of $AlCl_3$-CH_3NO_2 catalyst to benzyl chloride within the limits studied in the benzylation of benzene and toluene has no apparent effect on the intramolecular selectivity (isomer distribution). Intermolecular selectivity, as expressed by the k_T/k_B value, however, is seen to decrease slightly with increasing catalyst concentration. This latter trend seems to indicate that increasing the catalyst concentration increases the reactivity of the cationic species leading to lower substrate selectivity (smaller k_T/k_B value). On the other hand, the constancy of the intramolecular selectivity values seems to indicate that the formation of the various methyldiphenylmethanes depends on different factors than the ones influencing the k_T/k_B values. The explanation was made previously that k_T/k_B values are related to the rate of formation of the π complex whereas the isomer distributions are related to the stabilities of various σ complexes.

Effect of Solvent (Nitromethane) Concentration. Table III summarizes the data on the effect of changing the concentration of the solvent nitromethane relative

Table III. The Effect of Concentration of Solvent CH_3NO_2 Relative to $AlCl_3$ on the Competitive Benzylation of Toluene and Benzene[a]

Concn of $AlCl_3$ in CH_3NO_2 (% wt/wt)	k_T/k_B	—Distribution of isomers, %— Ortho	Meta	Para
20.0	5.6	42.4	6.1	51.5
10.0	5.4	42.4	6.2	51.4
1.3	4.6	42.7	6.2	51.2

[a] Molar ratio of the reactants toluene:benzene:benzyl chloride:$AlCl_3$ = 20:20:1:0.1 (50°, 5 min).

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(9) G. A. Olah and J. A. Olah, *J. Org. Chem.*, **32**, 1612 (1967).

(10) (a) L. Schmerling, *Ind. Eng. Chem.*, 40, 2072 (1948); (b) H. C. Brown and B. A. Bolto, *J. Amer. Chem. Soc.*, **81**, 3320 (1959).

to the catalyst aluminum chloride. The data show that while the isomer distribution is again unchanged, with excess nitromethane the intermolecular selectivity value (k_T/k_B) slightly diminishes. The same phenomenon has been observed in the benzylation of benzene and toluene with benzyl alcohol.[11]

Effect of the Concentration of Benzyl Chloride Relative to Aromatics. The concentrations of the catalyst and benzyl halide were generally kept low to avoid local overheating and overly rapid reactions. Table IV summarizes the results of benzylations in which the concentration of benzyl chloride was varied while all other factors remained constant. From the data it is clear that there is little effect observed. The data in Tables II–V indicate that substrate selectivity (k_T/k_B) is somewhat sensitive to the reaction conditions. However, the isomer distribution (intramolecular selectivity) is seen to be essentially independent of reaction conditions when nonisomerizing conditions are maintained.

Table IV. Effect of the Concentration of Benzyl Chloride Relative to Aromatics on the Competitive Benzylation of Toluene and Benzene[a]

Toluene: benzene: benzyl chloride (mol/mol)	k_T/k_B	—Distribution of isomers, %— Ortho	Meta	Para
20:20:1	5.4	42.4	6.2	51.4
15:15:1	5.2	41.6	5.9	51.9
10:10:1	5.0	41.6	5.8	52.6
5:5:1	5.1	42.0	6.1	51.9

[a] Molar ratio of reactants: toluene:benzene, 1:1; benzyl chloride:$AlCl_3$, 1:0.1; $AlCl_3$–CH_3NO_2 (20 wt/wt %) was used; 50°, 5 min.

The Effect of the Variation of Halogen in AlX_3–CH_3NO_2 and $C_6H_5CH_2X$. Table V lists the results of competitive benzylations using $AlCl_3$–CH_3NO_2 and $AlBr_3$–CH_3NO_2 as catalysts and benzyl fluoride, chloride, and bromide as alkylating agents. The data show that for a given aluminum halide (Cl or Br) k_T/k_B is smallest for benzyl fluoride and greatest for benzyl bromide. This is reasonable if the k_T/k_B value is inversely related to the amount of polarization of the benzyl halide–aluminum halide–CH_3NO_2 complex. The isomer distribution is seen, again, to be insensitive to the nature of the alkylating agent.

Table V. The Effect of Variation of Halogen in the Combination of AlX_3–CH_3NO_2 and Benzyl Halides on the Inter- and Intramolecular Selectivity of the Competitive Benzylation of Toluene and Benzene[a]

AlX_3	$C_6H_5CH_2X$	k_T/k_B	—Isomer distribution, %— Ortho	Meta	Para
Cl	F	3.3	41.2	5.8	53.0
Cl	Cl	5.4	42.4	6.2	51.4
Cl	Br	7.6	39.9	5.8	54.3
Br	F	3.3	40.7	5.7	53.7
Br	Cl	6.2	41.0	6.0	53.0
Br	Br	8.9	39.4	5.7	55.0

[a] Molar ratio of reactants: toluene:benzene:benzyl halide: AlX_3–CH_3NO_2 (20 wt/wt %), 20:20:1:0.1; 50° for 5 min.

The results again point up to the fact that intermolecular selectivity is more sensitive to the nature (activity and concentration) of the catalyst and of the benzylating agent than intramolecular selectivity (isomer distribution). Furthermore, by proper use of the competitive method, the relative activities of various Friedel–Crafts catalysts and alkyl halides can be determined.

Such studies are possible only if reactions are not diffusion controlled, *i.e.*, only under kinetic control and when no thermodynamically affected side reactions (*i.e.*, transalkylation and isomerization) occur. When no halogen exchange between the catalyst and the benzyl halide occurs, then for a given Friedel–Crafts benzylation reaction k_T/k_B should provide an accurate reflection of the activities of the catalysts employed. It also follows that the same intermolecular selectivity values (k_T/k_B) represent a measure of the reactivity of the electrophilic benzylating agent involved. The smaller the value of k_T/k_B, the more reactive the benzyl halide–metal halide complex.

Table VI summarizes the data from competitive benzylations of benzene and toluene with benzyl chloride at a reaction temperature of 50°. Spectroscopic grade benzene and toluene were dried over molecular sieves prior to use. In each reaction the ratio benzene: toluene:benzyl chloride:catalyst was kept constant at 20:20:1:0.1 mmol and only the nature of the specific catalyst was varied from run to run. Reaction mixtures were uniformly quenched with water and the organic material was extracted with ether, dried over anhydrous sodium sulfate, and analyzed by gas chromatography. Dicyclohexyl was used as an internal standard for the gas chromatographic analyses.

In the cases of $AlCl_3$, $AlBr_3$, AlI_3, $GaCl_3$, and $ZrCl_4$, significant amounts of *m*-methyldiphenylmethane and dimethyldiphenylmethane were found indicative of isomerization and transalkylation reactions, respectively. The occurrence of these side reactions means that k_T/k_B values in these cases are meaningless and were therefore not considered in Table VI. Antimony pentafluoride catalysts also bring about formation of some dimethyldiphenylmethane (transalkylation product) and apparently lead also to different amounts of intramolecular isomerization. The meaning of the numerical k_T/k_B value in this case is therefore somewhat in doubt, but was included in Table VII.

Based on the relationship between intermolecular selectivity (k_T/k_B) values and catalyst activity the following relative order of catalyst activity is indicated: $SbF_5 > SbF_5$–$CH_3NO_2 > AlCl_3$–$CH_3NO_2 > TaCl_5 > SbCl_5$–$CH_3NO_2 > AlBr_3$–$CH_3NO_2 > TiCl_4 > ZrI_4 > FeCl_3 > FeCl_3$–$CH_3NO_2 > ZrCl_4 > ZrBr_4 > SbCl_5 \gg SnCl_4 > AuCl$. This order seems to be in good agreement with literature[3d] data on the strengths of various catalysts.

Although the k_T/k_B values for the 29 catalysts compared vary from 3 to 10 the isomer distributions (intramolecular selectivity) are relatively constant (except, of course, those catalysts causing obvious extensive isomerization). This, we feel, strongly supports the suggestion that the nature of the benzyl chloride–metal halide complex is primarily determining intermolecular selectivity but is rather unimportant in affecting

(11) O. Tsuge, M. Tashiro, and A. Torii, *Kogyo Kagaku Zasshi*, **71**, 229 (1968).

Table VI. Inter- and Intramolecular Selectivity in the Competitive Benzylation of Toluene and Benzene with Benzyl Halides Catalyzed by Various Friedel–Crafts Catalysts at 50°[a]

Catalyst	$C_6H_5CH_2X$	Time, min	k_T/k_B	Isomer distribution, % Ortho	Meta	Para
$AlCl_3$[e]	Cl	1	f	18.0	58.0	24.0
$AlCl_3$–CH_3NO_2[b]	Cl	5	4.5	42.4	6.2	51.4
$AlBr_3$	Cl	1	f	12.3	61.6	26.1
AlI_3	Cl	1	f	29.9	25.7	44.4
$GaCl_3$	Cl	1	f	12.0	64.0	24.0
$TiCl_4$	Cl	5	6.0	41.0	4.5	54.5
SbF_5	Cl	5	3.9	42.5	8.1	49.4
SbF_5–CH_3NO_2[b]	Cl	5	4.2	43.2	6.3	50.6
$SbCl_5$	Cl	5	7.4	42.9	6.1	51.0
$SbCl_5$–CH_3NO_2[b]	Cl	5	6.0	41.6	5.7	52.7
$SbCl_5$	F	5	3.5	47.2	5.0	47.8
$SbCl_5$	Br	5	7.7	42.7	2.9	54.5
$ZrCl_4$	Cl	0.5	6.9	42.2	5.3	52.6
$ZrCl_4$	Cl	1	6.9	42.2	5.5	53.3
$ZrCl_4$	Cl	10	f	31.3	18.6	50.2
$ZrCl_4$	Cl	30	f	19.4	40.2	40.4
$ZrBr_4$	Cl	1	7.1	40.9	5.2	53.9
$ZrBr_4$	Br	1	9.4	38.0	4.9	57.1
$ZrBr_4$	F	1	3.2	39.8	9.0	51.2
ZrI_4	Cl	1	6.2	41.1	5.4	53.6
ZrI_4	F	1	3.1	40.0	9.3	50.7
$FeCl_3$	Cl	5	6.9	41.0	5.7	53.3
$FeCl_3$	F	5	3.5	42.8	5.8	51.4
$FeCl_3$–CH_3NO_2[c]	Cl	5	6.5	41.8	6.1	52.1
$SnCl_4$	Cl	60	9.8	41.5	6.6	51.9
$AuCl_3$	Cl	60	10.2	42.7	6.0	51.3
SbF_5–FSO_3H[d]	Cl	1	3.6[f]	40.8	11.0	48.1
SbF_5–FSO_3H[d]	Br	1	2.1[f]	27.1	32.4	40.5
SbF_5–FSO_3H[d]	F	1	2.1[f]	38.9	16.9	44.2

[a] Mole ratio of reactants: toluene:benzene:benzyl halide:catalyst = 20:20:1:0.1. [b] 20 wt %. [c] $FeCl_3$; 160 mg/4 ml of CH_3NO_2. [d] 1:1 "magic acid" was used. [e] From O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jap.*, **40**, 119 (1967). [f] Due to obvious isomerization (disproportionation) could not be determined.

the isomer distributions. In addition to the found order of catalytic activity, our studies indicate that for a given catalyst the order of reactivity of benzyl halide is $C_6H_5CH_2F > C_6H_5CH_2Cl > C_6H_5CH_3Br$.

In comparing the data of Table VII, when using the neat metal halide catalyst in aromatic hydrocarbon media the systems are frequently not completely homogeneous, due to the limited solubility of the catalysts. It is interesting to note that the isomer distribution for benzylations with $FeCl_3$ (partially heterogeneous conditions) and $FeCl_3$–CH_3NO_2 (strictly homogeneous reaction) are virtually identical (see Table VI). The k_T/k_B values (6.8 and 6.5, respectively) likewise are very similar. Such data lead us to conclude that isomerization and/or transalkylation in Friedel–Crafts benzylation is frequently not caused by a lack of a strictly homogeneous nature of the solutions, and is mainly a function of the nature of the benzylating agent and catalyst system involved.

II. Benzylation of Benzene with Methylbenzyl Chlorides Catalyzed by Various Lewis Acids. Classification of Catalysts According to Their Activity in Benzylation Reactions. For many years attempts were made to establish the order of activity of various metal halides (Lewis acids) as catalysts in Friedel–Crafts reactions. As an example we have considered the order of catalyst activity based on intermolecular selectivity (k_T/k_B) values, as described in Part I. One must note that since in all likelihood no simple monotonic order of catalytic activity is involved in Friedel–Crafts reactions,[12] meaningful data are difficult to obtain. We feel, however, that if all reaction parameters (reaction time and temperature, concentration of catalyst, benzyl halide, and aromatic substrate, work-up, and analytical procedures) were kept constant, with the exception only of the nature of the metal halide catalyst, then one can obtain indication of an order of catalytic activity of Friedel–Crafts catalysts.

Tsuge and Tashiro[13] reported the benzylation of benzene with *p*-chlorobenzyl chloride under the influence of some Friedel-Crafts catalysts. $AlCl_3$ and $GaCl_3$ led to formation of large amounts of diphenylmethane and *m*-chlorodiphenylmethane, indicating substantial intra- and intermolecular isomerization (transbenzylation). With such catalysts as $AlCl_3$–$C_6H_5NO_2$, $GaCl_3$–$C_6H_5NO_2$, $CaCl_3$–CH_3NO_2, and $FeCl_3$, the only reaction product observed was *p*-chlorodiphenylmethane; thus no apparent isomerizing conditions prevailed.

In order to compare the catalytic activity of a wider variety of Friedel–Crafts catalysts we studied the benzylation of benzene with methylbenzyl chlorides. All benzylations were run at 25° using spectroscopic grade benzene and redistilled methylbenzyl chlorides. Conditions were kept strictly constant for each run: [benzene] = 20.0 *M*, [methylbenzyl chloride] = 1.0 *M*, [catalyst] = 0.1 *M*, and 0.50 g of dicyclohexyl as an internal standard material. Samples were uniformly quenched with water and the organic layer was extracted with ether, dried over anhydrous Na_2SO_4, and analyzed by means of gas chromatography. The

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(12) G. A. Olah in "Friedel-Crafts and Related Reactions," Vol. I, Wiley-Interscience, New York, N. Y., 1963, Chapter XI.

(13) O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jap.*, 40, 119 (1967).

Table VII. Benzylation of Benzene with Methylbenzyl Chlorides under the Influence of Various Friedel–Crafts Catalysts at 25° for 10 min[a]

No.	Catalyst	Isomeric $CH_3C_6H_4$-CH_2Cl	Total conversion, %	Rel yield, % DPM[b]	Rel yield, % Me-DPM[b]	Isomeric Me-DPM Ortho	Isomeric Me-DPM Meta	Isomeric Me-DPM Para	Group of periodic table
1	BCl_3	m	1.8		100		100		IIIa
2	BCl_3	p	2.7		100			100	IIIa
3	BI_3	p	5.5		100			100	IIIa
4	$AlCl_3$ CH_3NO_2	p	55.7		100			100	IIIa
5	$AlCl_3$	p	77.0	92.7	7.3	2.5	84.6	12.9	IIIa
6	$AlCl_3$	m	52.6	81.0	19.0	3.4	89.1	7.5	IIIa
7	$AlCl_3$	o	73.2	89.0	11.0	4.4	82.5	13.1	IIIa
8	$AlBr_3$	p	90.0	92.0	8.0	8.7	70.4	20.9	IIIa
9	$AlBr_3$	m	83.9	93.2	6.8	9.3	69.2	20.5	IIIa
10	AlI_3	p	77.6	77.8	22.2	9.6	70.9	19.5	IIIa
11	AlI_3	m	77.1	70.4	29.6	7.6	74.2	18.2	IIIa
12	AlI_3	o	58.3	82.1	17.9	18.4	61.1	20.5	IIIa
13	$GaCl_3$	p	86.6	93.4	6.6	10.6	64.9	24.5	IIIa
14	$GaBr_3$	p	89.6	93.6	6.4	8.9	65.9	25.2	IIIa
15	GaI_3	p	59.6	19.0	81.0	7.0	18.3	74.7	IIIa
16	$GaCl_2$	p	82.8	47.3	52.7	10.0	61.7	28.3	IIIa
17	$GaCl_2$	m	74.5	63.0	37.0	0.1	72.1	19.8	IIIa
18	$InCl_3$	p	11.1		100			100	IIIa
19	$InCl_3$	m	1.2		100		100		IIIa
20	$InCl_3$	o	6.5		100	100			IIIa
21	$InBr_3$	p	33.8		100			100	IIIa
22	InI_3	p	30.8		100			100	IIIa
23	$SnCl_4$	m	1.3		100		100		IVa
24	$SnCl_4$	o	2.0		100	100			IVa
25	$TiCl_4$	p	35.5		100			100	IVb
26	$TiCl_4$	m	2.5		100		100		IVb
27	$TiCl_4$	o	11.4		100	100			IVb
28	$TiBr_4$	m	6.6		100		100		IVb
29	$ZrCl_4$	m	25.0		100		100		IVb
30	$HfCl_4$	p	38.2		100			100	IVb
31	$HfCl_4$	m	48.4	1.8	98.2		95.1	4.9	IVb
32	$HfCl_4$	o	32.1		100	100			IVb
33	$HfBr_4$	p	35.5	2.3	97.7	0.6	2.6	96.8	IVb
34	HfI_4	p	97.3	93.7	6.3	8.9	68.1	23.0	IVb
35	SbF_5	p	85.6	35.9	64.1	7.4	24.0	68.6	Va
36	SbF_5	m	38.7		100		99.8	0.2	Va
37	$SbCl_5$	p	54.2		100			100	Va
38	$SbCl_5$	m	37.2		100		100		Va
39	$SbCl_5$	o	42.1		100	100			Va
40	NbF_5	m	78.5	8.1	90.9		86.1	13.9	Vb
41	$NbCl_5$	p	60.2	4.4	95.6	3.6	6.2	90.2	Vb
42	$NbCl_5$	m	36.4		100		100		Vb
43	TaF_5	m	59.9	8.4	92.6	2.6	94.9	2.5	Vb
44	TaF_5	o	75.5	55.0	45.0	27.8	60.2	12.0	Vb
45	$TaCl_5$	p	39.3	5.4	94.6	6.2	9.2	84.6	Vb
46	$TaCl_5$	m	33.1	1.9	98.1		97.2	2.7	Vb
47	$TaBr_5$	p	41.4	1.8	98.2	1.7	3.5	94.8	Vb
48	MoF_6	m	42.9		100		100		VIb
49	$MoCl_5$	p	25.4		100			100	VIb
50	$MoCl_5$	m	42.0	1.3	98.7	1.9	98.1		VIb
51	WCl_6	m	11.0		100		100		VIb
52	$ReCl_3$	p	2.2		100			100	VIIb
53	$ReCl_3$	m	2.2		100		100		VIIb
54	$ReCl_5$	m	14.2		100		100		VIIb
55	$FeCl_3$	p	34.4		100			100	VIII
56	$FeCl_3$	m	37.0		100		100		VIII
57	$FeCl_3$	o	70.5		100	100			VIII
58	$FeCl_2$	p	2.6		100			100	VIII
59	$FeCl_2$	m	1.0		100		100		VIII
60	$PtCl_4$	p	1.3		100			100	VIII

[a] Molar ratio of reactants: benzene:methylbenzyl chloride:catalyst = 20:1.0:0.1. [b] DPM, diphenylmethane; MeDPM, methyldiphenylmethane.

data for these reactions are summarized in Table VII (in which inactive catalysts are not included).

Based on the data in Table VII it seems possible to classify Friedel–Crafts catalysts for benzylation reaction as: A, very active, with attendant intra- and intermolecular isomerizations; B_1, moderately active, without side reactions; B_2, weak; C, very weak or inactive.

It is clear that the group IIIa metal (B, Al, Ga, In) halides (except the fluorides) all show catalytic activity in the methylbenzylation reaction (no. 1–22). Aluminum and galium halides (no. 5–17) are strong cata-

Table VIII. Classification of Friedel–Crafts Catalysts Based on Their Activity in Benzylation Reactions

Group A, Very Active

Catalysts which bring about high yields in the benzylation reactions, but at the same time cause extensive intra- and intermolecular isomerizations: $AlCl_3$, $AlBr_3$, AlI_3, $GaCl_3$, $GaCl_2$, $GaBr_3$, GaI_3, $ZrCl_4$, $HfCl_4$, $HfBr_4$, HfI_4, SbF_5, NbF_5, $NbCl_5$, TaF_5, $TaCl_5$, $TaBr_5$, MoF_6, $MoCl_5$

Group B_1, Moderately Active

Bring about high yields of benzylation with no extensive accompanying side reactions (isomerizations): $InCl_3$, $InBr_3$, InI_3, $SbCl_5$, WCl_6, $ReCl_5$, $FeCl_3$, $AlCl_3$–RNO_2, $AlBr_3$–RNO_2, $GaCl_3$–RNO_2, SbF_5–RNO_2

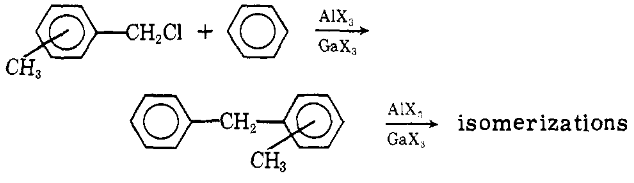
Group B_2, Weak

Bring about low yields of benzylation with no side reactions: BCl_3, BBr_3, BI_3, $SnCl_4$, $TiCl_4$, $TiBr_4$, $ReCl_3$, $FeCl_2$, $PtCl_4$

Group C, Very Weak or Inactive

These catalysts were found inactive (or gave less than 1% products) for benzylations under the reaction conditions used: BF_3, SbF_3, $SbCl_3$, $SbBr_3$, SbI_3, $AsBr_3$, AsI_3, $BeCl_2$, BiF_3, $BiCl_3$, BiI_3, $CdCl_2$, CdI_2, $CeBr_3$, $CsCl$, $CsBr$, CsI, $CrBr_3$, CrI_3, $CrCl_2$, $CoCl_2$, $CoBr_2$, CoI_2, Cu_2Cl_2, Cu_2Br_2, Cu_2I_2, $CuCl_2$, $DyCl_3$, $ErCl_3$, ErI_3, HfI_4, $EuCl_3$, $CdCl_3$, CdI_3, $GeCl_4$, GeI_4, $AuCl_3$, $IrCl_3$, $LaCl_3$, PbF_2, $PbCl_2$, $PbBr_2$, PKI_2, $LuCl_3$, $MgCl_2$, $MgBr_2$, MgI_2, $MnCl_2$, $MnBr_2$, MnI_2, $HgCl_2$, $HgBr_2$, HgI_2, $NdCl_3$, NdI_3, $NiCl_2$, NiI_2, $OsCl_3$, $OsCl_4$, $PdCl_2$, $PtCl_2$, $PrCl_3$, $PrBr_3$, $RhCl_3$, $RuCl_3$, $SmCl_3$, $ScCl_3$, $ScBr_3$, $SrCl_2$, $SnCl_2$, $SnPr_2$, SnI_2, SnI_4, $TiCl_3$, TiI_4, $TeCl_4$, $TbCl_3$, $TmCl_3$, VCl_4, VF_4, $YbCl_3$, YCl_3, $ZnCl_2$, $ZnBr_2$, ZnI_2, ZrI_4, $WoCl_3$, VCl_4

lysts (group A, *vide supra*) which bring about intra- and intermolecular isomerizations of the first formed methyldiphenylmethanes.[14] Indium halides are quite active and boron halides are moderately active catalysts in benzylations producing methyldiphenylmethanes. Side reactions are not involved here.



Of the group IVa elements (C, Si, Ge, Sn, Pb), only the halides of tin show slight catalytic activity. The IVb metal (Ti, Zr, Hf) halides are becoming increasingly more powerful catalysts with increasing molecular weight and size of halogen. Hafnium iodide, in fact, is a very powerful catalyst both for benzylation and subsequently for intra- and intermolecular isomerization (no. 34).

Although antimony pentafluoride is as strong (or stronger) a catalyst as aluminum, galium, hafnium, and zirconium halides (no. 35 and 36), antimony pentachloride is considerably less reactive (no. 37–39). The group Vb metal (Nb, Ta) halides show very powerful catalytic and isomerization activity (no. 40–47). The halides of group VIb (Mo, W) are also powerful catalysts.

Finally, the halides of groups VIIb (Re) and VIII (Fe, Pt) show moderate activity for catalyzing the benzylation reaction without attendant side reactions.

From the data presented in Tables V, VI, and VII, we can classify Friedel–Crafts catalysts for the benzylation reactions with respect to activity and selectivity in four groups, as shown in Table VIII. This classification compares well with other empirical catalyst reactivity sequences in the literature[12] for other types of Friedel–Crafts reactions.

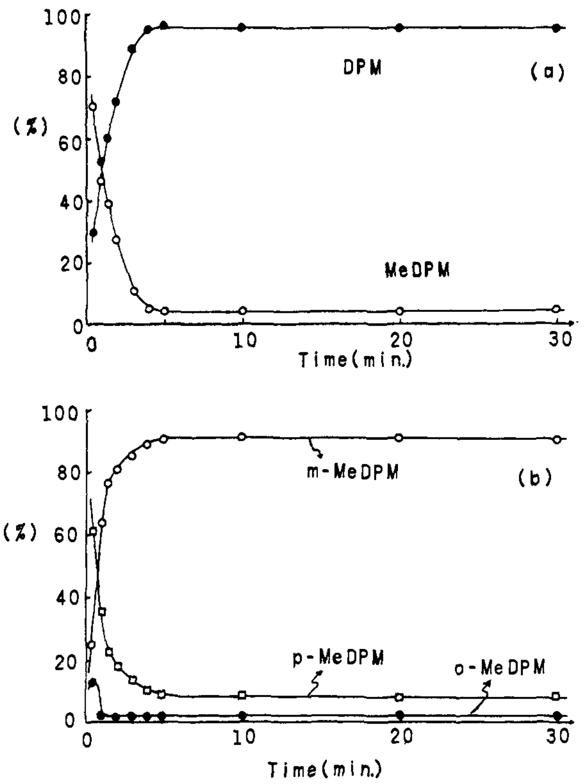


Figure 1. Benzylation of benzene with *p*-methylbenzyl chloride in the presence of aluminum chloride catalyst at 25°: (a) distribution of products; (b) isomer distribution of methyldiphenylmethanes.

III. Aluminum Chloride Catalyzed Benzylation of Benzene with Methylbenzyl Chlorides. Intra- and Intermolecular Isomerization. Aluminum chloride is a very active (group A type) catalyst both for benzylation and for subsequent intra- and intermolecular isomerization. We, therefore, were interested in how the $AlCl_3$-catalyzed reaction proceeds starting from *o*-, *m*-, or *p*-methylbenzyl chloride, respectively, as the benzylating agent of benzene. The molar ratio of the reactant, [benzene]:[methylbenzyl chloride]:[$AlCl_3$] = 20:1.0:0.1, was employed. The reactions were carried out with vigorous stirring at 25° and followed by periodical sampling. In Figures 1–3, the distribution of the products (a series) and the isomer distribution of methyldiphenylmethanes (b series) are shown, respectively. All reactions were practically completed within 10 min, giving rise to almost the same product distributions (diphenylmethane (DPM)–methyldiphenylmethane (MeDPM) ratio and predominant meta isomer of methyldiphenylmethane) regardless of starting methylbenzyl chloride isomer employed. It seems that both intra- and intermolecular isomerizations are taking place simultaneously. The mechanism of the isomerizations is considered[14] to involve the identical benzenium ion type intermediate.

In these reaction mixtures there were no detectable amounts of dimethyldiphenylmethanes formed. This finding indicates that the cleavage reaction of protonated methyldiphenylmethane intermediates takes place

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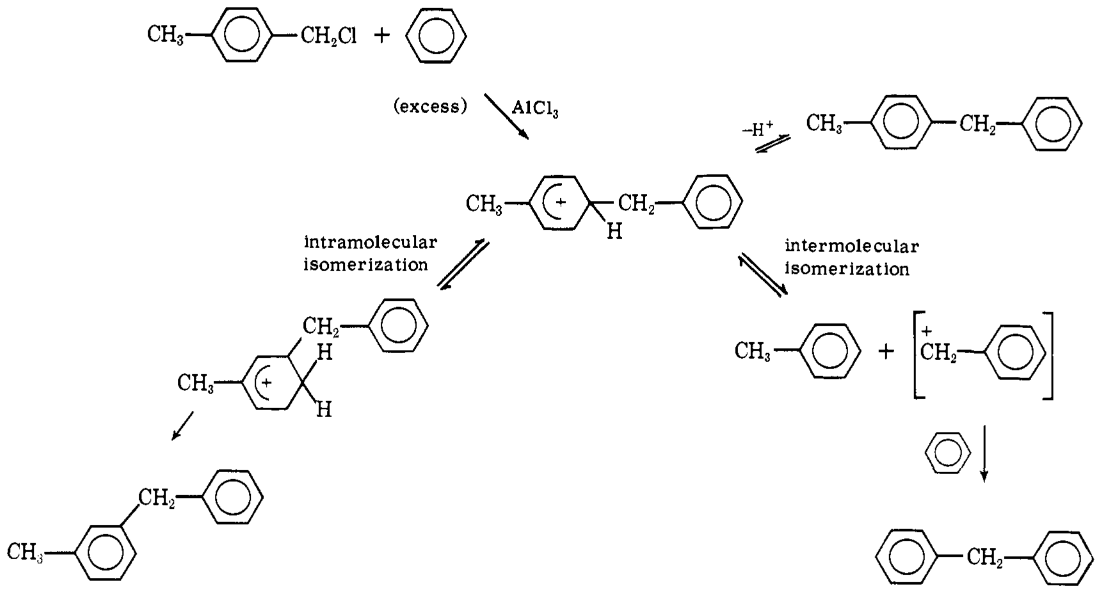
(14) In fact, treatment of methyldiphenylmethane in excess benzene with $AlCl_3$ and/or $GaCl_3$ leads to the production of diphenylmethane; see ref 13. Aluminum chloride is also an effective catalyst for intramolecular isomerization of isomeric methyldiphenylmethanes; see ref 9.



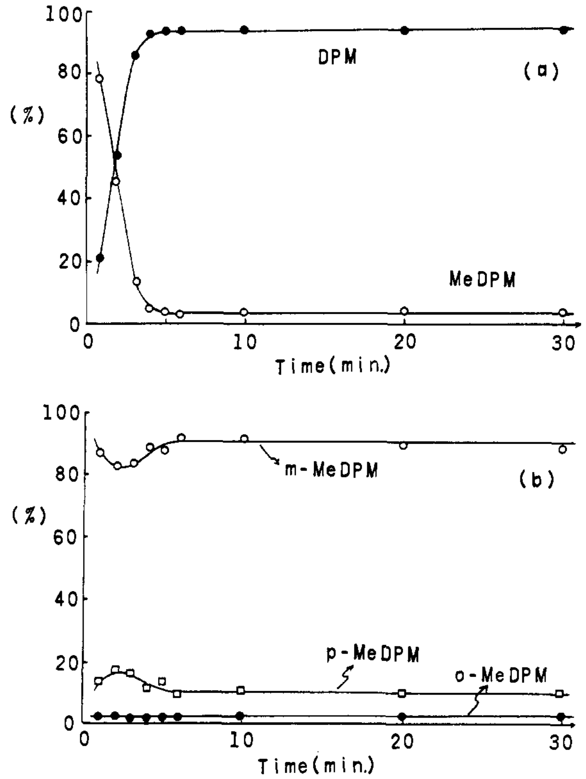


Figure 2. Benzylation of benzene with *m*-methylbenzyl chloride in the presence of aluminum chloride catalyst at 25°: (a) distribution of products; (b) isomer distribution of methyldiphenylmethanes.

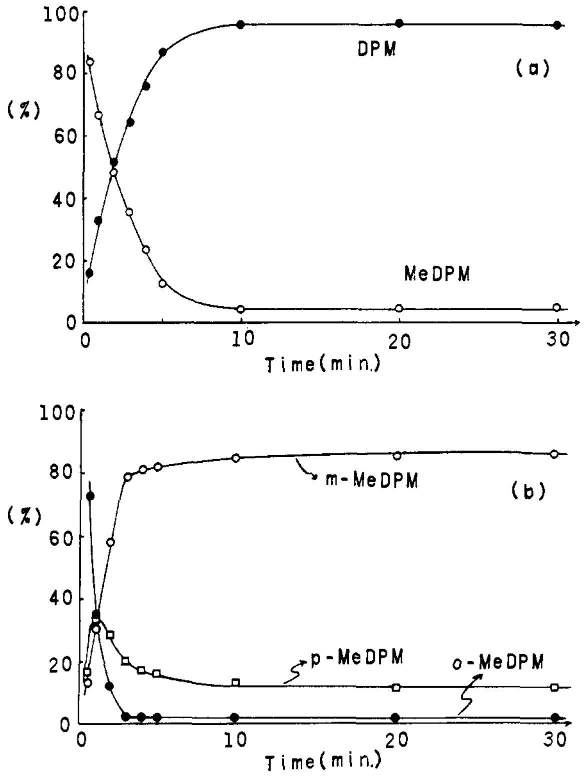


Figure 3. Benzylation of benzene with *o*-methylbenzyl chloride in the presence of aluminum chloride catalyst at 25°: (a) distribution of products; (b) isomer distribution of methyldiphenylmethanes.

predominantly in the manner to give toluene and benzyl cation (and not benzene and methylbenzyl cations).

In contrast to neat aluminum chloride, a strongly isomerizing group A type catalyst, its nitromethane complex, $CH_3NO_2 \cdot AlCl_3$, is a relatively mild group B type catalyst. In previous benzylation studies[5c] we have utilized this much milder catalyst.

IV. Substituent Effects in the Competitive Benzylation of Benzene and Toluene with Substituted Benzyl Chlorides. The competitive method of rate determination can be employed only if the observed relative rates are indeed first-order dependent upon the concentration of the competing aromatic substrates (benzene and toluene) and the product distributions are obtained under kinetically controlled conditions (free of isomerizations), *i.e.*, independent of the reaction time. These prerequisites clearly indicate the suitability of using group B (B_1 or B_2) type catalysts over group A or C type catalysts (as classified in Table VIII). Based on this consideration we have chosen titanium tetrachloride as a catalyst for the competitive benzylation of benzene and toluene. Titanium tetrachloride shows moderate catalytic activity and readily gives homogeneous reaction systems because of its fairly good solubility in aromatics.

Evidence for the first-order dependence of the

Table IX. $TiCl_4$-Catalyzed Competitive Benzylation of Changing Ratios of Benzene and Toluene with Benzyl Chloride at 30°

Toluene : benzene ratio	Obsd k_T/k_B	k_T/k_B according to first-order dependence on aromatics
5:1	29.8	5.9
3:1	17.9	6.0
1:1	6.3	6.3
1:3	2.2	6.6
1:5	1.4	7.0
		Av 6.4

benzylation reactions in aromatics is given in Table IX. Changing the concentration of either of the aromatic components in the competitive benzylation of toluene and benzene from a 1:1 ratio to 5:1 and 1:5 showed that the k_T/k_B value remains almost unchanged if a first-order dependence of the aromatics is accepted.

Based on the observed isomer distribution of the $TiCl_4$-catalyzed benzylations (Tables VI and VII) it is believed that practically nonisomerizing and therefore only kinetically controlled reaction conditions were present for all of the competitive benzylations described below. In addition, the nonisomerizing conditions have been experimentally proved by using *m*-methylbenzyl chloride as the competitive benzylating agent (Table X), as the k_T/k_B values and isomer distributions were found to be independent of the reaction time.

Experience gained with nonisomerizing reaction conditions discussed above allowed us to carry out competitive $TiCl_4$-catalyzed benzylations with benzyl and substituted benzyl chlorides. Table XI summarizes the results of substituent effects in competitive benzylations of benzene and toluene.

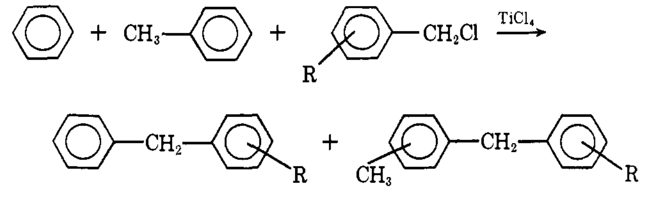
In these experiments all parameters are kept constant and only the nature of the attacking species (benzyl cation entity) is changed systematically through substituents in the benzyl chlorides. Data of Table XI prove the effect of substituents both on substrate selectivity (as reflected in the k_T/k_B rate ratios) and on positional selectivity (as shown by isomer distributions, primarily the ortho:para ratios). Electron-donating substituents ortho and para to the benzylic center increase the k_T/k_B ratio and at the same time decrease the ortho:para isomer ratio in the methyldiphenylmethanes formed, *e.g.*, para substitution is becoming predominant. On the other hand, electron-withdrawing substituents decrease k_T/k_B and increase the ortho:para isomer ratio. Meta substituents have relatively little effect.

Table X. $TiCl_4$-Catalyzed Competitive Benzylation of Benzene and Toluene with *m*-Methylbenzyl Chloride at 30°[a]

Reaction time, min	Products, mol %		k_T/k_B	Isomer distribution of Me_2DPM, %		
	m-MeDPM	Me_2DPM		3–2′	3–3′	3–4′
2	11.8	88.2	7.5	41.0	2.6	56.4
5	11.9	88.1	7.4	40.9	2.7	56.4
10	11.4	88.6	7.8	41.3	2.5	56.2
15	11.4	88.6	7.8	41.2	2.3	56.5
20	11.5	88.5	7.7	41.3	2.4	56.3

[a] The ratio of reaction components was [benzene]:[toluene]:[*m*-methylbenzyl chloride]:[$TiCl_4$] = 10:10:1:0.1.

Table XI. $TiCl_4$-Catalyzed Benzylation of Benzene and Toluene with Benzyl and Substituted Benzyl Chlorides at 30°[a]



R of $RC_6H_4CH_2Cl$	k_T/k_B	Methyldiphenylmethane isomer, % Ortho	Meta	Para	½ ortho: para
p-NO_2[b]	2.5	59.6	6.2	34.2	0.87
o-F	4.8	39.3	7.8	52.9	0.37
m-F	4.6	37.7	7.8	54.5	0.35
p-F	8.7	43.0	6.5	50.5	0.43
m-CF_3	5.1	38.4	9.6	52.0	0.41
o-Cl	4.6	38.8	7.2	54.0	0.36
m-Cl	5.5	43.1	6.5	50.4	0.43
p-Cl	6.2	40.1	5.0	54.9	0.37
H	6.3	40.5	4.3	55.2	0.37
o-CH_3	19.1	24.6	3.4	72.0	0.17
m-CH_3	7.8	41.3	2.5	56.2	0.37
p-CH_3	29.0	31.4	2.1	66.5	0.24
2,4,6-$(CH_3)_3$	37.4	16.1	3.1	80.8	0.10
o-CH_3O	60.3	23.2	1.3	75.5	0.15
m-CH_3O	13.2	47.5	2.3	50.2	0.47
p-CH_3O	97.0	28.6	1.5	69.9	0.20
2,4,6-$(OCH_3)_3$3,5-$(CH_3)_2$	136.0	18.3	1.1	80.6	0.11

[a] The ratio of reaction component was [benzene]:[toluene]:[benzyl chloride]:[$TiCl_4$] = 10:10:1:0.1. [b] The k_T/k_B value was obtained from the analysis by gas–liquid chromatography. The isomer distribution data were obtained after the reduction of the products (see Experimental Section).

Experimental data clearly indicate that with decreasing electrophilicity of the reagent the transition state increasingly resembles the Wheland intermediate. As the para-substituted benzenium ion has greater stability than the ortho substituted ion (meta being the least stable), para substitution is becoming predominant, 66.5–80.8% (with k_T/k_B being as high as 136). The incipient benzyl cation (*e.g.*, the benzyl chloride–catalyst complex) is a strong electrophile; thus k_T/k_B and isomer distribution obtained in the reaction of unsubstituted benzyl chloride itself with benzene and toluene indicate an early transition state, resembling starting materials (toluene or benzene) and not the benzenium ion intermediates. Consequently, k_T/k_B is low and the ½ ortho:para isomer ratio is relatively high (although due to some bulkiness of the reagent complex the ortho:para ratio is not as high as values found with smaller strong electrophiles, where the ½ ortho:para ratio can reach or exceed 1).

One of the most important factors to influence both the substrate and positional selectivity is the nature of the electrophile, which together with the nature of

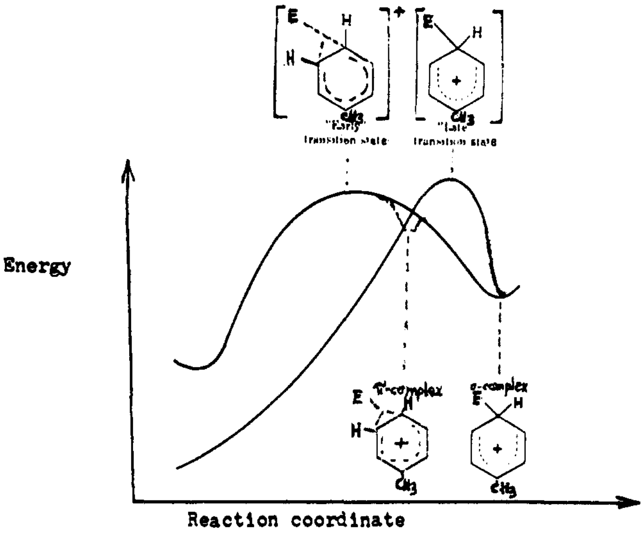
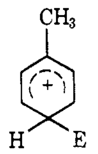


Figure 4. (a) Potential energy curve (left side) of reaction with early transition state resembling starting aromatics (π complex); (b) potential energy curve (left side) of reaction with late transition states resembling the σ complex. For simplicity the proton elimination side of the reaction is not shown.

the substrate, determines the position of the transition state. Steric effects, of course, can also play an important role in determining positional selectivity.

The position of the transition state in electrophilic aromatic substitutions is thus obviously not a rigidly fixed one always resembling the Wheland intermediate (arenium ion, σ complex) as generally assumed, but frequently lies much earlier on the reaction coordinate of the potential energy diagram of the reaction, resembling not the intermediate but the starting aromatics (oriented π complex or aronium ion involving two-electron, three-center bond formation with the electrophile).[15] This is in accordance with the concept of "Hammond's postulate"[16] as applied to electrophilic aromatic substitutions.



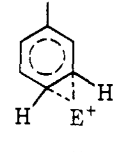
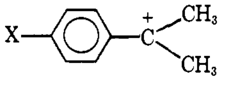
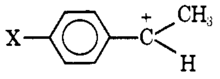


Figure 4 depicts the potential energy curves schematically for the "early" and "late" transition states, respectively. The proton elimination side is not shown in these diagrams for simplicity. Figure 4 on the left side shows the energy profile in cases where low substrate but high positional selectivities are operative. For such reactions (like p-nitrobenzylation in this work), the transition state lies early on the reaction path and resembles a benzonium ion (oriented π complex). Whether or not there is a separate π-complex minimum (corresponding to an intermediate) following the transition state of highest energy, thus separated by a second, but lower energy maximum from the arenium ion (σ complex) intermediate, cannot be answered at this time, but should not affect the path of the reaction (taking into consideration the tetracoordinated benzonium ion nature of the π-type transition state, with substantial orientation already present; see subsequent discussion). On the other hand, Figure 4, on the right side, shows the energy profile in cases where the late transition state is of a predominant benzenium ion (σ complex) nature (as in para methoxybenzylation).

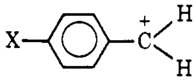
It is possible to obtain further evidence that the nature of electrophiles plays a most important role in determining the substrate selectivity, by correlating k_T/k_B values of benzylation with the ^{13}C chemical shifts of the carbenium centers of the corresponding benzyl cation. Although only few primary benzyl cations were directly observed as stable species so far,[17] the ^{13}C chemical shifts of several additional primary benzyl cations can be estimated by extrapolation of available data of tertiary cumyl **1**, secondary styryl **2**, and primary benzyl **3** cations. It was already established in previous work[17a] that $\Delta\delta^{13}C$(tertiary–secondary) for ions **1**-X compared with **2**-X remains essentially the same (20–21 ppm) as X is varied and amounts to a methyl substituent effect as compared to hydrogen. In addition, the ^{13}C shift value for **3**-OCH$_3$ ($\delta^{13}C^+ = 25$ ppm)[17] was obtained, which leads to the ^{13}C shift difference, $\Delta\delta^{13}C$ (secondary–primary), of 30 ppm. Assuming that the shift differences of the methoxy-substituted cations, *i.e.*, $\Delta\delta^{13}C$ (secondary–primary) and $\delta^{13}C$ (tertiary–primary) (30 and 50 ppm, respectively), can be applied for other substituents, X makes it possible to calculate the $^{13}C^+$ chemical shifts of **3**-X which are shown in Table XII, together with the reported data of **1**-X, **2**-X, and **3**-OCH$_3$.[17]



1-X



2-X



3-X

Plotting log (k_T/k_B) *vs.* $\delta^{13}C$ of benzyl cations results in a good linear relationship as shown in Figure 5.

Table XII. Carbon-13 Chemical Shifts[a] of the Carbenium Centers in Cumyl, Styryl, and Benzyl Cations

	$\delta^{13}C^+$ of **1**	$\delta^{13}C^+$ of **2**	$\delta^{13}C^+$ of **3**
p-OCH$_3$	−25[b]	−5[b]	25[d]
2,4,6-(CH$_3$)$_3$		−18[b]	12[e]
p-CH$_3$	−49[b]	−28[b]	2[e]
p-F	−53[c]		3[e]
H	−61[b]	−40[b]	−10[e]
m-F	−68[c]		−18[e]

[a] All chemical shifts relative to $^{13}CS_2$ in parts per million. [b] See ref 22a. [c] See ref 22b. [d] See ref 22c. [e] Calculated value.

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[15] For a general definition of the concept of carbocations and differentiation of benzonium ions from benzenium ions, see: G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

[16] G. S. Hammond, *ibid.*, **77**, 334 (1955).

[17] (a) G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971); (b) G. A. Olah, C. L. Jeuell, and A. M. While, *ibid.*, **91**, 3961 (1969); (c) G. A. Olah and R. D. Porter, *ibid.*, **93**, 6877 (1971).

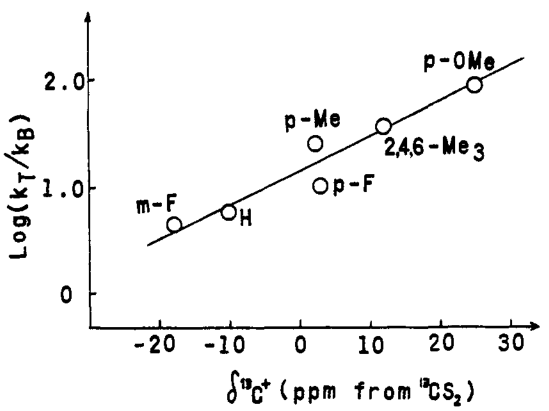


Figure 5. Correlation of log (k_T/k_B) values with ^{13}C chemical shifts of carbenium centers of substituted benzyl cations.

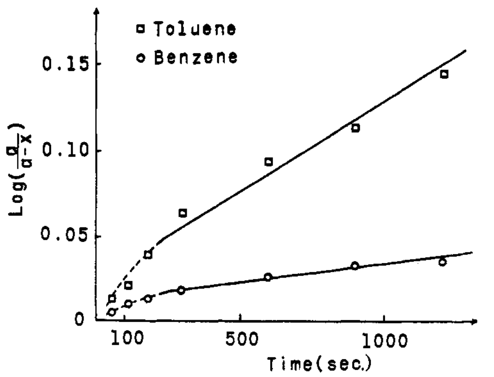
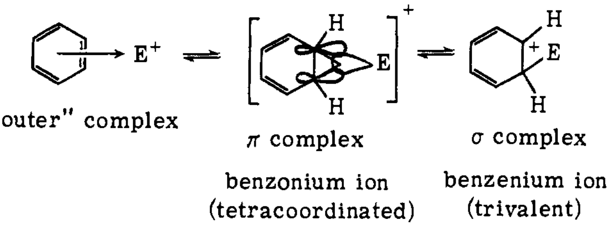


Figure 6. Pseudo-first-order plot of $TiCl_4$-catalyzed benzylation of toluene and benzene at 30°.

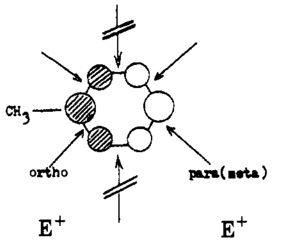
This strongly indicates that the substrate selectivity (k_T/k_B values) in benzylations is closely related to the electrophilic nature of the intermediate benzyl cations.

In the interaction of an electrophile with an aromatic substrate first a weak reagent–substrate complex (outer complex[18]) is formed. The formation of such complexes is reversible and does not lead to substituted products. Aromaticity is not lost in such complexes, as indicated by spectroscopic studies (like works of Zollinger[19] and Nakane[20]) showing only slight changes in the aromatic substrates.

As the reagent moves closer to bonding distance, the highest lying occupied aromatic π orbital containing an electron pair overlaps with the empty orbital of the electrophile, forming a two-electron three-center bond (π complex). The formed complex is indeed a bridged tetracoordinated carbonium ion (benzonium ion).[15] Opening of the three-center bond of the benzonium ion leads to the trivalent benzenium ion (σ complex) which frequently can be directly observed.



Concerning the directing effect, as in the case of the methyl group in toluene, consideration of the symmetry of the highest occupied molecular orbital (HOMO) involved in the interaction with the electrophile (E^+) gives good indication. As interaction can take place only on bonds formed by orbitals bearing the same sign, *i.e.*, 1–2, 1–6, 3–4, and 4–5, but not 2–3 and 5–6, attack on the two former can lead only to ortho substitution, whereas the latter will give para- (and less meta-) substituted products.



V. Intermolecular Kinetic Selectivity. Proof from Noncompetitive Rate Study of the Benzylation of Toluene and Benzene, and Comparison with Competitive Rate Data.

Due to the generally unreliable kinetic behavior of Friedel–Crafts systems very few kinetic rate studies of alkylations were ever undertaken. However, the relative reactivities of toluene and benzene in a number of alkylations were measured by Brown and his coworkers.[21] We have also reported previously the relative reactivities (obtained by competitive experiments) of the same substrates in benzylation,[5c] isopropylation,[22a] and *tert*-butylation[22b] under reaction conditions considered kinetically controlled (nonisomerizing). In addition, we reported[5d] evidence that k_T/k_B values for these reactions obtained from noncompetitive kinetic rate studies of the substrates (in separate experiments) are in good agreement with those obtained from competitive experiments.

We wish to report new additional experimental proof for the $TiCl_4$-catalyzed benzylations showing that results of kinetic rate studies (noncompetitive method) give toluene:benzene rate rates (k_T/k_B) in good agreement with data obtained by use of the competitive method described previously in this paper. Rates of $TiCl_4$-catalyzed benzylation of toluene and benzene, respectively, with benzyl chloride in excess aromatics as solvent were measured separately at 30°. A known amount of dicyclohexyl was used as an internal standard. Conditions were kept strictly identical in all runs ([aromatic], 200 mmol; [benzyl chloride], 10.0 mmol; [$TiCl_4$], 1.0 mmol).

Pseudo-first-order rate plots were obtained (see Figure 6) assuming $d[\text{product}]/dt = k[TiCl_4][\text{aromatic}]\cdot[\text{benzyl chloride}]$ and that [$TiCl_4$] stays constant. All aromatics were used in large excess; thus $d[\text{product}]/dt = k'[\text{benzyl chloride}]$, where $k' = k[TiCl_4][\text{aromatic}]$.

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[18] Using Mulliken's definition: R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[19] M. Christen, W. Koch, W. Simon, and H. Zollinger, *Helv. Chim. Acta*, **45**, 2077 (1962).

[20] R. Nakane, A. Natsubori, and O. Kurihara, *J. Amer. Chem. Soc.*, **87**, 3597 (1965); **88**, 3011 (1966); R. Nakane, T. Oyama, and A. Natsubori, *J. Org. Chem.*, **33**, 275 (1968); **34**, 949 (1969); R. Nakane and T. Oyama, *J. Phys. Chem.*, 70, 1146 (1966).

[21] (a) H. C. Brown and C. R. Smoot, *J. Amer. Chem. Soc.*, **78**, 6245, 6255 (1956); (b) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959); (c) H. C. Brown and M. Grayson, *ibid.*, **75**, 6285 (1953).

[22] (a) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuk, *ibid.*, **86**, 1046 (1964); (b) G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964).

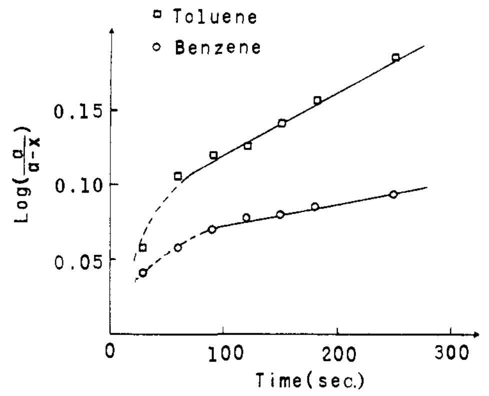


Figure 7. Pseudo-first-order plot of benzylation of toluene and benzene with antimony pentachloride catalyst in nitromethane solution at 30°.

Table XIII. Rate Constants of Benzylation of Toluene and Benzene with Benzyl Chloride

Aromatic	Catalyst	Reaction temp, °C	Rate constant, sec^{-1}
Benzene	$TiCl_4$	30	5.1×10^{-5}
Toluene	$TiCl_4$	30	2.8×10^{-4}
Benzene	$SbCl_5$-CH_3NO_2	30	3.2×10^{-4}
Toluene	$SbCl_5$-CH_3NO_2	30	8.7×10^{-4}
Benzene[a]	$AlCl_3$-CH_3NO_2	25	2.2×10^{-4}
Toluene[a]	$AlCl_3$-CH_3NO_2	25	7.7×10^{-4}

[a] Taken from data of ref 5d.

Table XIV. Relative Reactivities of Toluene and Benzene in Benzylation with Benzyl Chloride and Isomer Distribution of Methyldiphenylmethanes

Catalyst	Temp, °C	Noncompetitive data	Competitive data	Isomer distribution (%) of methyldiphenylmethane from competitive benzylation: Ortho	Meta	Para
$TiCl_4$	30	5.5	6.3 (5.9)[a]	40.5	4.3	55.2
$SbCl_5$-CH_3NO_2	30	2.7	2.6	42.9	4.7	52.3
$AlCl_3$-CH_3NO_2[b]	25	3.45	3.20	43.5	4.5	52.0

[a] The value obtained from the same reaction conditions used for the noncompetitive method containing dicyclohexyl in the system. [b] Taken from our previous data, ref 5d.

In plotting log $a/(a - x)$ *vs.* time a stands for the initial concentration of benzyl chloride and x is the concentration of the product diphenylmethane.

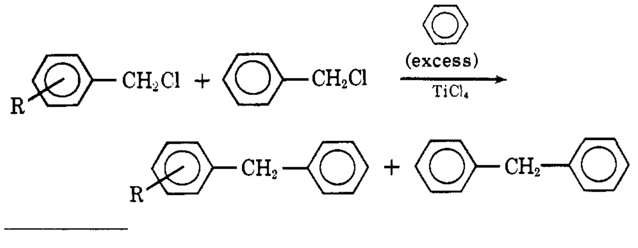
Similarly, we undertook the kinetic study of the $SbCl_5$-catalyzed benzylation of toluene and benzene, at 30° in nitromethane solution using again a known amount of an internal standard (*m*-nitrotoluene) in the separate kinetic experiments. Strictly identical reaction conditions were used for all runs ([aromatic], 100 mmol; [benzyl chloride], 5.0 mmol; [$SbCl_5$], 1.7 mmol; [CH_3NO_2], 0.828 mol). Pseudo-first-order plots obtained are shown in Figure 7.

In both the $TiCl_4$- and $SbCl_5$-catalyzed reactions, the systems are homogeneous and we obtained well-reproducible first-order rate constants from the slope of the kinetic curves which are summarized along with our previous data[5d] in Table XIII (all data are the average of three parallel determinations). We wish to stress that although in the present study of benzylation of toluene and benzene, strictly identical conditions were used but still not necessarily under well enough reproducible conditions to claim absolute rate data of general validity. It is considered, however, that uncertainties due, for example, to small impurities in the systems, should cancel out sufficiently in the parallel experiments to allow calculation of relative toluene: benzene rate ratios from individual kinetic data.

The relative reactivities of benzylation of toluene and benzene (k_T/k_B) calculated from the ratios of separate rate determinations of toluene and benzene are shown in Table XIV compared with previously reported data. The comparison of data in Table XIV indicates that the k_T/k_B values in the investigated benzylation are satisfactory in the limit of the experimental error in both competitive and noncompetitive determinations. The isomer distributions show little difference in the three catalyst systems.

VI. Substituent Effects in the Benzylation of Benzene with Substituted Benzyl Chlorides. Attempt to Obtain Ortho-Substituent Constants. Brown and Grayson[21c] reported the kinetic study of the $AlCl_3$-$C_6H_5NO_2$-catalyzed benzylation of aromatics with 3,4-dichlorobenzyl chloride and *p*-nitrobenzyl chloride in nitrobenzene solutions but they failed to measure the rate of benzylation with benzyl chloride and *p*-chlorobenzyl chloride because of too rapid reaction. However, Tsuge and Tashiro[13] reported that *p*-chlorobenzyl chloride shows only half the reactivity of benzyl chloride itself in $InCl_3$-catalyzed reactions, determined by the competitive method. This result suggests that the Hammett ρ–σ relationship could be applied to the benzylation reactions. In fact, recently Shimao[23] reported that a Hammett–Brown ρ–σ^+ relationship was observed in the benzylation reaction of toluene with several substituted benzyl alcohols in the presence of *p*-toluenesulfonic acid as catalyst.

In order to obtain more detailed information about the Hammett ρ–σ relationship and particularly in an attempt to apply it to ortho-substituted systems the $TiCl_4$-catalyzed benzylation of benzene with substituted benzyl chlorides was investigated in competitive benzylation of benzene with benzyl chloride and substituted benzyl chlorides.



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(23) I. Shimao, *Nippon Kagaku Zasshi*, **89**, 895, 1259 (1968).

As discussed previously, titanium tetrachloride can be advantageously used as a relatively mild nonisomerizing (group B_2) catalyst. In order to maintain suitable conditions for the competitive rate determinations the conversions of benzyl chloride were usually kept less than 10% with reaction times of 5–15 min. Data of Table XV clearly indicate that the relative rate ratio (k_R/k_H, benzylation rate of benzene with substituted benzyl chloride relative to the rate with parent benzyl chloride) can be obtained by the competitive method since a first-order dependence on benzyl chloride is established.

Table XV. The Catalyzed $TiCl_4$ Competitive Benzylation of Benzene with Substituted and Parent Benzyl Chloride at 30°[a]

R of $RC_6H_4CH_2Cl$	$RC_6H_4CH_2Cl$: $C_6H_5CH_2Cl$ ratio	Obsd k_R/k_H	k_R/k_H according to first-order dependence in chlorides
m-CH_3	1:3	0.42	1.25
	1:1	1.36	1.36
	3:1	3.81	1.27
			Av 1.29
p-Cl	1:3	0.06	0.19
	1:1	0.21	0.21
	3:1	0.51	0.27
			Av 0.22
o-Cl	1:3	0.02	0.06
	1:1	0.08	0.08
	3:1	0.21	0.07
			Av 0.07

[a] The molar ratio of reaction component was [benzene]:[benzyl chloride]:[$TiCl_4$] = 20:1:0.1.

The k_R/k_H values thus obtained by the competitive method are summarized in Table XVI for ten benzyl chloride derivatives. The noncompetitive method of rate determination also gave relative rate values of *p*-fluorobenzyl chloride and benzyl chloride ($k_{p\text{-F}}/k_H$ = 1.16) within the experimental error, comparing well with the competitive determination ($k_{p\text{-F}}/k_H$ = 1.29).

Table XVI. The Catalyzed $TiCl_4$ Competitive Benzylation of Benzene with Benzyl and Substituted Benzyl Chlorides at 30° and Brown's σ^+ Constants Calculated from Data. σ^+ Ortho Values for Ortho Fluoro, Chloro, and Methyl Groups

R of $RC_6H_4CH_2Cl$	k_R/k_H	$\sigma_{m,p}^{+b}$	σ_o^{+c}
o-F	0.15		0.31
m-F	0.08	0.35	
p-F	1.29 (1.22)[a]	−0.07	
o-Cl	0.07		0.33
m-Cl	0.06	0.40	
p-Cl	0.22	0.11	
H	1.0	0.0	
o-CH_3	3.23		−0.19
m-CH_3	1.29	−0.07	
p-CH_3	12.4	−0.31	

[a] From noncompetitive experiments (see Experimental Section). [b] Taken from ref 3c. [c] Calculated from eq 7 in this work.

Previous studies of substituent constants such as Brown's σ^+ data were generally obtained by comparing substituent effects in the substrates). Due to the interference by steric effects ortho substituent effects could previously not generally be obtained. In our studies we compared substituents in the benzylating agent; thus steric effects should not be imposed. We, therefore, attempted to obtain from benzylation data suitable relationships to allow determination of ortho-substituent effects.

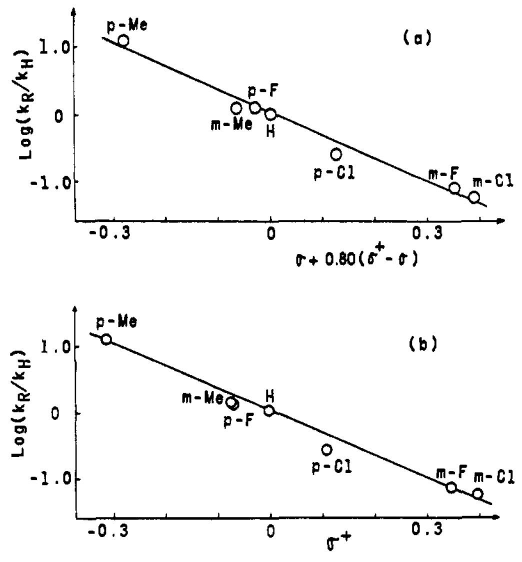

Figure 8. Relationships between (a) log (k_R/k_H) and $\sigma + 0.80(\sigma^+ - \sigma)$ values and (b) log (k_R/k_H) and σ^+ constants, for benzylation of benzene with meta- and para-substituted benzyl chlorides.

When applying the Yukawa–Tsuno equation[24] to plot log (k_R/k_H) *vs.* $\sigma + 0.80(\sigma^+ - \sigma)$ values of meta and para substituent groups, such as meta and para methyl, meta and para chloro, and meta and para fluoro, a linear relationship was obtained for given substituents as shown in Figure 8a. This relationship leads to the following equation

$$\log (k_R/k_H) = -3.6[\sigma + 0.80(\sigma^+ - \sigma)] \qquad (1)$$

We subsequently plotted log (k_R/k_H) *vs.* σ^+ values for the substituents and obtained a good linear correlation as well. Figure 8b gives the following relationship

$$\log (k_R/k_H) = -3.3\sigma^+ \qquad (2)$$

The Yukawa–Tsuno equation (1) did not give a better correlation than eq 2 for the present study, which may be ascribed to the γ value of 0.80. Yukawa and Tsuno[24] discussed that only in reactions having γ within 0.7–1.3 would Brown and Okamoto's equation be apparently successful. We think the present study represents such a case.

Changing the nature of electrophiles causes a shift in the position of the transition state of highest energy along the reaction coordinate which reflects the change of the substrate selectivity. However, such a shift of the position of the transition state must be relatively small when the nature of electrophile is changed to a small extent as in the present case where the benzyl cationic species are changed through substituents from para methyl to meta chloro. This may be the reason why Figures 8a and b did not make a significant difference, in spite of the fact that we expected the Yukawa–

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(24) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 971 (1959).

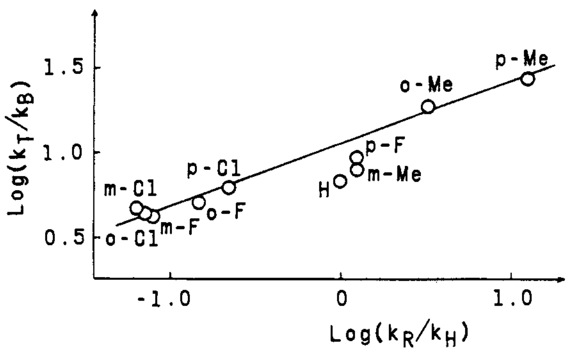

Figure 9. Relationship between log (k_T/k_B) and log (k_R/k_H) for benzylation.

Tsuno treatment would give a better correlation for the present study.

Unfortunately, we were unable to measure the $k_{p\text{-OCH}_3}/k_H$ value because *p*-methoxybenzyl chloride itself is too reactive and causes the production of dimethoxyldiphenylmethane derivatives.

When comparing log (k_T/k_B) and log (k_R/k_H) values a linear relationship was observed as shown in Figure 9. Although some deviations are seen, it should be noted that ortho substituent groups give an especially good linear correlation. From Figure 9 eq 3 can be

$$\log (k_T/k_B) = 0.36 \log (k_R/k_H) + 1.05 \qquad (3)$$

obtained. Now we can use eq 2 instead of eq 1 without any significant difference for the above mentioned reason. Equations 2 and 3 give

$$\log (k_T/k_B) = -1.19\sigma^+ + 1.05 \qquad (4)$$

Equation 4 indicates that the k_T/k_B value can be recognized as a function of σ^+ value in general use. Since the steric effects of ortho groups seem to be almost (but not necessarily completely) compensated in the benzylation reactions, we attempted to obtain σ_o^+ values for the studied substituent groups.

Equation 4 is further modified to eq 5. The σ^+

$$\sigma^+ = \frac{\log (k_T/k_B) - 1.05}{-1.19} \qquad (5)$$

values of ortho methyl, chloro, and fluoro groups were calculated from eq 5 using the corresponding k_T/k_B values of Table XI and are listed in Table XVI. If one allows extrapolation of eq 5 to the methoxyl group, it gives a calculated $\sigma^+_{o\text{-OCH}_3}$ value of -0.61.

In spite of extensive study on the nature of the ortho effects,[25] it has not yet led to an understanding of the many complex factors involved in ortho substituent effects. However, the present study may offer an example to obtain ortho substituent constants which, of course, reflect the overall effects. In order to examine the general validity of these values, however, further detailed studies will be necessary. One approach pursued in our laboratories is a comparison of ^{13}C nmr shifts in substituted stable benzyl cations of the carbenium carbon centers as a function of ring substituents.[16] Assuming additivity of the substituent effects a good linear correlation is observed, indicating that the $\sigma^+_{o\text{-CH}_3}$ -0.19 value is reasonable.

Conclusions

Through the systematic study of substituent effects on the benzylation of toluene and benzene with substituted benzyl chlorides, the present work provides substantial understanding of the general mechanistic aspects of electrophilic aromatic substitution reactions. In electrophilic aromatic substitutions the position of the transition is not a fixed one. It can lie late on the reaction coordinate and resemble the intermediate (σ complex) as reflected by high k_T/k_B rate ratios and low ortho/para ratios in our ratios (para substitution becoming increasingly predominant, due to the highest stability of the para-substituted benzenium ion) or it can be an "early" one resembling starting aromatics (π complex) reflected by low k_T/k_B rate ratios and high ortho:para isomer ratios (in accordance with charge distribution of the aromatics).

The relative reactivities of toluene and benzene (k_T/k_B) in the $TiCl_4$-catalyzed benzylations are in good agreement, within experimental error, as determined in both competitive and noncompetitive rate studies. Thus, diffusion or encounter controlled and therefore nonkinetic conditions cannot be considered as responsible for the observed low substrate selectivities.[26] We feel, therefore, that our conclusions reached some years ago relating to the concept of low substrate but high positional selectivity electrophilic aromatic substitutions are correct.

In order to explain the low substrate but high positional selectivities observed in a series of electrophilic aromatic substitutions, we previously suggested that in these reactions the transition state of highest energy leads to formation of an oriented π complex in the substrate selectivity determining step, followed by formation of σ complexes for the ortho, para, and meta positions, which differ substantially in energy.

We suggested this mechanistic concept making the generally accepted assumption that π complexes were, indeed, intermediates. This left us no alternative but to consider two distinct intermediates, π and σ complexes, with the corresponding separate transition states leading to these complexes. The recently developed general concept of carbocations[15] clearly defines π complexes as tetracoordinated aronium ions. As our continued experimental work[27] and recent theoretical calculations[28-30] provide no evidence for aronium ion intermediates, there is no obvious necessity to involve separate aronium ion intermediates (although their existence cannot be definitely excluded). The nature of the transition state can be different from the intermediate, as the position of the transition state in electrophilic aromatic substitutions is not a fixed one. In reactions with relatively weak electrophiles, or in reactions with weakly basic aromatics, the transition state can lie "late" on the reaction coordinate, resembling the intermediate σ complexes. In reaction with strongly electrophilic reagents, or with strongly basic aromatics, it lies *early*, resembling starting aro-

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(25) M. Charton, *J. Org. Chem.*, 34, 278 (1969), and references given therein.

(26) For a review of some of the controversy which arose concerning low substrate but high positional selectivity aromatic substitutions see ref 4.

(27) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, in press.

(28) E. Helgstand, *Acta Chem. Scand.*, 24, 3687 (1970).

(29) W. Yakubetz and P. Schuster, *Angew. Chem., Int. Ed. Engl.*, 40, 497 (1971).

(30) W. J. Hehre and J. A. Pople, personal communication.

matics, thus being more of π-complex (arenium ion) nature (whether or not separated from the arenium ion (σ complex) intermediate by a distinguishable second energy mininum (*i.e.*, π intermediate)).

Experimental Section

Materials. The benzene, toluene, and nitromethane used were commercial products of spectrograde. Benzyl halides and substituted benzyl chlorides were commercially available materials of highest purity.

***o*-Methylbenzyl chloride** was prepared by chlorination of commercial *o*-methylbenzyl alcohol with dry hydrogen chloride in ether solution at 0°, bp 115–120° (11 mm).

***m*-Methylbenzyl chloride** was prepared in a similar fashion, bp 120–124° (18 mm).

2,4,6-Trimethoxy-3,5-dimethylbenzyl chloride was prepared from 1,3,5-trimethoxy-2,4-dimethylbenzene, which was obtained according to the procedure as reported[31] for the preparation of 2,6-dimethoxytoluene. 2,4,6-Trimethoxytoluene (0.1 mol) was added to 200 ml of phenyllithium (0.1 mol) in ether solution. After standing for 2 days at room temperature in the dark, dimethyl sulfate (0.12 mol) was added to the ether solution, refluxed for 2 hr, and poured into ice–water. The product was extracted with ether and isolated as a white solid, mp 60°. 1,3,5-Trimethoxy-2,4-dimethylbenzene thus obtained was chloromethylated with 37% formalin-concentrated hydrochloric acid in dioxane solution with introduction of dry hydrogen chloride at 50–55° for 1 hr.[32] The reaction mixture was then poured into ice–water, extracted three times with ether, and distilled to give a clear, but viscous liquid, bp 97–98° (0.03 mm), which solidified on standing at room temperature, mp 57–58°. The structure was compared by analysis and its pmr system.

All of the anhydrous Lewis acid halides were commercially available (Research Organic/Inorganic Chemical Co.) and used without further purification.

General Procedure for Competitive Benzylation. (a) With Aluminum Chloride–Nitromethane Complex Catalyst. Benzene (156 g, 2.0 mol) and toluene (184 g, 2.0 mol) were mixed, and to the equimolar aromatic solution 0.10 mol of the benzyl halide was added. In another vessel, cooled in an ice bath, 20 g of aluminum halide (I, Br, Cl) was slowly added with stirring to 80 g of nitromethane. A reaction flask containing 5 g of the benzene–toluene–benzyl halide solution was placed into a constant temperature bath at 50°. This solution was stirred vigorously for 10 min. Then the calculated amount of the 20% (wt/wt) aluminum halide–nitromethane solution (10 molar % *vs.* the benzyl halide) was added at once to the reaction flask. The reaction mixture was stirred at 50° for the desired time and then quenched with ice–water. The organic layer was extracted with ether, a known amount of the internal standard material was added, and the solution was dried over Na_2SO_4 and analyzed by gas–liquid chromatography.

(b) With Titanium Tetrachloride Catalyst in Excess Aromatics as Solvent. To an equimolar mixture of benzene (0.1 mol) and toluene (0.1 mol), 0.001 mol of titanium tetrachloride was added. To the resulting homogeneous solution was added, in a constant temperature bath, dropwise and with good stirring, 0.01 mol of (substituted) benzyl chloride over a period of 3 min and reaction was allowed to proceed further for another 10 min. It was then poured into ice–water, extracted with ether, dried over Na_2SO_4, concentrated, and analyzed by gas–liquid chromatography.

(c) Competitive $TiCl_4$-Catalyzed Benzylation of Benzene with Parent and Substituted Benzyl Chlorides. Into a mixture of 0.2 mol of benzene and 0.001 mol of titanium chloride, a mixture of an equimolar amount (0.01) of benzyl chloride and a substituted benzyl chloride was added at once with vigorous stirring at 30°. The reaction was allowed to proceed for 5–15 min generally to keep the conversion of both of the benzyl chlorides lower than 10%; the mixture was then quenched with ice–water, extracted with ether, dried over Na_2SO_4, and analyzed by gas–liquid chromatography.

Conversion of *p*-Nitrobenzyltoluenes to Methyldiphenylmethanes. Nitrodiphenylmethane derivatives could not generally be analyzed directly by gas chromatography; thus it was necessary to convert them prior to analyses to the corresponding diphenylmethane derivatives.

A mixture of approximately 2 mmol of *p*-nitrobenzyltoluenes, 6 mmol of stannous chloride hydrate,[33] and 4 g of concentrated hydrochloric acid was placed at 0° in a flask fitted with a thermometer and reflux condenser, and then heated on the steam bath to 80° and kept for 20 min. The solution was cooled in an ice-water bath, neutralized with 30% sodium hydroxide solution, and extracted three times with ether. Evaporation of solvent gave the corresponding anilines, as confirmed by ir and nmr spectroscopic analyses. The *p*-aminobenzyltoluenes were diazotized at 5–10° by treating a mixture of 1 mmol of amines, 0.2 g of concentrated hydrochloric acid, and 3 g of water with 2 mmol of sodium nitrite in 1 g of water. The solution was then added to 10 g of 30% hypophosphorus acid solution[34] and placed in a refrigerator overnight. The reaction mixture was extracted with ether, dried (Na_2SO_4), concentrated, and analyzed by gas–liquid chromatography.

General Procedures for Kinetic Studies. (a) With Titanium Tetrachloride Catalyst. Exactly 3.0 mol of purified benzene (or toluene) and 15.0 mmol of titanium tetrachloride were mixed. To the mixture was added 2.0 g of dicyclohexyl as an internal standard and 3.0 mmol of water to provide a known uniform amount of possible major impurity. Into 15.9 g (in case of benzene) of the above solution kept at 30°, 10.0 mmol of benzyl chloride was added at once with vigorous stirring. Samples were withdrawn periodically, quenched with ice–water, extracted with ether, dried (Na_2SO_4), concentrated, and analyzed with gas–liquid chromatography.

The same procedure was used for the reaction of *p*-fluorobenzyl chloride with benzene. Pseudo-first-order rate plots were obtained to give the rate constant, $k = 6.3 \times 10^{-5}\ \text{sec}^{-1}$. Calculation gave a relative rate, $k_{p\text{-F}}/k_{\text{H}}$, of 1.22 ($6.3 \times 10^{-5}\ \text{sec}^{-1}/5.1 \times 10^{-5}\ \text{sec}^{-1}$) which is listed in Table XVI.

(b) With Antimony Pentachloride–Nitromethane Catalyst. To the mixture of 100 mmol of toluene, 5.0 g of antimony pentachloride–nitromethane solution (10 wt/wt %, 1.7 mmol as $SbCl_5$), 45 g of nitromethane, and 0.50 g of *m*-nitrotoluene (as an internal standard), was added at once 5.0 mmol of benzyl chloride in 1.0 g of nitromethane at a constant temperature of 30° while maintaining vigorous stirring. Sampling, work-up, and analytical procedures were taken in the same manner as given in a.

Analytical Procedure. The analyses of all products were carried out by gas–liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph equipped with a hydrogen flame ionization detector system and open tubular capillary columns. Peak areas were obtained with an Infotronics Model CRS-1 electronic printing integrator.[35]

Acknowledgment. Support of our work by a grant from the Petroleum Research Fund, administrated by the American Chemical Society, is gratefully acknowledged.

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[31] J. P. Lambooy, *J. Amer. Chem. Soc.*, **78**, 771 (1956).

[32] G. J. Lestina and H. W. J. Cressman, *J. Org. Chem.*, **25**, 1453 (1960).

[33] C. W. Ferry, J. S. Buck, and R. Baltzly, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 239.

[34] See N. Kornblum in ref 33, p 295.

[35] Table XVII, showing characteristic retention times of diphenylmethane derivatives, the type of Golay capillary columns employed, and column temperatures, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7448. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.