TABLE II

EXTRACTION AND GAS CHROMATOGRAPHY DATA

Ether	pK_a	% H_2SO_4 at pK_a	K_D'[a]	Slope of log plot[a]	Concn. of stock soln., vol. %	Column[b] packing	Column temp., °C.	Flow rate, ml./min.
Hexamethylene oxide	−2.02	33	68	0.88	1.5	T	106	60
Tetrahydrofuran	−2.08	35	2.65	.92	2	P	63	90
2,5-Dimethyltetrahydrofuran								
cis	−2.44	40	25.0	.80	4	P	50	120
trans	−2.65	43	29.5	.84	4	P	50	120
2-Methyltetrahydrofuran	−2.65	43	6.60	.86	2	P	68	70
Tetrahydropyran	−2.79	43	14.0	.76	2	T	82	80
7-Oxa[2.2.1]bicycloheptane	−2.80	44	6.27	.93	2	P	82	96
Dioxane	−3.16	48	0.21	.83	1	T	90	75

[a] See ref. 6 for the meaning of these symbols. Conditions for extraction and gas chromatography are the same as in previous papers: cyclohexane as solvent, Burrell K-2 Kromotog with 6-foot column and helium as carrier gas. [b] Burrell Corp. packings: P, polyethylene glycol on Celite; T, Tween on Celite.

TABLE III

SOLVENT EXTRACTION OF THF FROM CYCLOHEXANE AT 20°

% H_2SO_4	H_0	D	$\log \frac{D}{(K_D' - D)}$	pK_a
18.40	−1.00	2.480	1.140	−2.14
24.97	−1.34	2.334	0.548	−1.89
33.69	−1.95	1.950	.190	−2.14
35.24	−2.07	1.429	.131	−2.20
39.70	−2.39	1.034	− .563	−1.83
43.54	−2.74	0.798	− .731	−2.01
46.82	−3.06	.598	− .804	−2.26
48.84	−3.26	.486	− .832	−2.43

aide.[31] It was purified by distillation until homogeneous to gas chromatography. 2,5-Dimethyltetrahydrofuran was made by the cyclization of hexane-2,5-diol using the method of Reynolds and Kenyon.[32]

When this was subjected to gas chromatography under the conditions given in Table II, two cleanly separated peaks of equal size were obtained corresponding to the *cis* and *trans* isomers. This offered the opportunity of measuring the basicities of the two compounds without actually separating them. The results of this study are presented in Fig. 4 in the form of the customary plot[6] of $\log [D/(K_D' - D)]$ *versus* H_0. The material with the longer retention time was assigned the *cis* configuration in view of its lower K_D' value. According to our previous observations[6] this indicates that it also has a lower parachor and, if the empirical relationship of Gillespie, Macbeth and Mills[33] holds here, it may be taken to be the *cis* isomer.

It is clear from this example that if it is possible to find a g.l.c. column which permits resolution of a group of volatile bases it is practical to determine their basicities simultaneously by the extraction method without separating the individual bases beforehand.

In Table III are presented typical data for determination of the pK_a of THF oxonium ion.

---

[31] A. Kirrmann and N. Hamaide, *Bull. soc. chim. France*, 789 (1957).

[32] D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **72**, 1593 (1950).

[33] D. T. C. Gillespie, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 280 (1940).

[CONTRIBUTION NO. 54 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

Aromatic Substitution. X.[1] The $AlCl_3 \cdot CH_3NO_2$-Catalyzed Benzylation of Benzene and *n*-Alkylbenzenes with Benzyl Chloride in Nitromethane Solution

BY GEORGE A. OLAH, STEPHEN J. KUHN AND SYLVIA H. FLOOD

RECEIVED OCTOBER 25, 1961

Competitive $AlCl_3 \cdot CH_3NO_2$-catalyzed benzylation of benzene and *n*-alkylbenzenes with benzyl chloride in homogeneous nitromethane solution has been investigated. Relative reactivities and isomer distributions were determined by gas–liquid chromatography, using when necessary a Golay type capillary column and hydrogen flame ionization detector. The observed relative rates, the reactions being first order in aromatic hydrocarbons, show good correlation with relative π-complex stabilities of alkylbenzenes, but not with σ-complex basicities. In the investigated low substrate selectivity reactions the amount of *meta* isomer formed was as low as 3.5 and not larger than 8.6%. Partial rate and selectivity factors are not applicable to the present systems (primary competition takes place between the π-electron systems of competing molecules as entities). The benzylation of benzene-d_6 shows a small secondary, direct kinetic isotope effect. The mechanism of the reaction is discussed in the light of the experimental results.

Introduction

The mechanism which for a long time was generally accepted for Friedel–Crafts type alkylation with alkyl halides involved ionization of the alkyl halide under the influence of the "acid" catalyst followed by electrophilic substitution of the aromatic nucleus by the carbonium ion.[2] A fundamental kinetic study by Brown and Grayson[3] of the reaction of benzyl halides with various aromatic compounds under the catalytic influence of aluminum chloride in nitrobenzene solution revealed that the reaction is third order—first order in aromatic component, first order in aluminum chloride and first order in the benzyl halide. Both benzyl chloride and *p*-chlorobenzyl chloride were found to react too rapidly for convenient rate measurement. Therefore 3,4-dichloro- and

---

[1] Part IX, *J. Am. Chem. Soc.*, **83**, 4581 (1961).

[2] C. C. Price, *Chem. Revs.*, **29**, 37 (1941); "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., pp. 1–82.

[3] H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953).

p-nitrobenzyl chloride which reacted at more convenient rates were primarily utilized in kinetic studies. The rate was found to increase with increasing basic properties of the aromatic component, the relative rate constant being

Aromatic	Relative rate
Chlorobenzene	0.47
Benzene	1.00
Toluene	1.64
m-Xylene	2.08

Unfortunately, there was no mention of the isomer distribution of the formed alkyldiphenylmethanes. Based on the kinetic data, Brown suggested that a concerted displacement mechanism involving nucleophilic attack by the aromatic component on the alkyl halide:aluminum chloride addition compound is consistent with the observations. The displacement mechanism suggested by Brown offered also 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. The displacement mechanism was found of general applicability for the explanation of the mechanism of Friedel–Crafts alkylations with primary halides. In later studies Brown and Bolto[4] determined the relative rate and isomer distribution in the gallium bromide catalyzed benzylation of benzene and toluene, using excess aromatics as solvent. Under the influence of gallium bromide, benzyl bromide undergoes an exceedingly rapid reaction with benzene and toluene. Attempts to measure the individual reaction rates failed. Utilizing a competitive method the relative rate of benzylation of toluene and benzene at 25° was established as 4.0. The isomer distribution in the benzylation of toluene exhibited marked variation with the reaction times, even when these were quite short. The observed isomer distribution values with reaction times of 10, 0.09, 0.03, 0.01 sec. were extrapolated to zero reaction time to obtain the isomer distribution for non-isomerizing conditions. These data provided only a fair fit with the selectivity relationship of Brown.[5]

ISOMER DISTRIBUTION AND PARTIAL RATE FACTORS IN THE BENZYLATION OF TOLUENE WITH BENZYL BROMIDE AND GALLIUM BROMIDE AT 25° AFTER BROWN AND BOLTO[4]

	Reacn. time, sec.	% Isomer distribution, %		
		ortho	*meta*	*para*
	10	23.1	45.7	31.2
	0.09	33.8	31.4	34.8
	.03	38.7	22.6	38.7
	.01	40.2	21.1	38.7
Extrap.	.00	41.1	19.4	39.5

Partial rate factors

$k_{\text{toluene}}:k_{\text{benzene}} = 4.0$ $o_f = 4.9$ $m_f = 2.3$ $p_f = 9.4$

Only rather recently has the Friedel–Crafts alkylation of alkylaromatics come to be considered a typical electrophilic aromatic substitution. Previously the alkylation reaction was believed to produce a typical isomer distribution.[6] The propylation of toluene was frequently reported to yield *p*-cymene uncontaminated by *o*- or *m*-cymene.[7] As late as 1954 this claim was made.[8] Several alkylations were reported in which the proportion of *meta* substitution obtained was anomalously large for an electrophilic reaction.[9] H. C. Brown has suggested that the substantial proportion of *m*-isopropyltoluene obtained by the propylation of toluene is due to the low selectivity of the reaction for the activated *o*- and *p*-positions of toluene.[10]

An isomer distribution obtained by alkylation can change due to positional isomerization under the Friedel–Crafts reaction conditions. Indeed, since the intermediate σ-complex postulated for alkylation is identical to that postulated for isomerization,[11] it is questionable that alkylation exclusive of isomerization is possible.

Alkylation reactions carried out using only excess of aromatic hydrocarbons as solvents are particularly sensitive to isomerizations. It seemed to be of interest to reinvestigate the benzylation of benzene, toluene and other alkylbenzenes in homogeneous systems using a suitable solvent capable of what was hoped, providing non-isomerizing conditions.

Results

The method of competitive relative rate determination was used in order to establish the relative reactivities of *n*-alkylbenzenes and benzene in the $AlCl_3 \cdot CH_3NO_2$-catalyzed benzylation with benzyl chloride in nitromethane solution. The addition complex $AlCl_3 \cdot CH_3NO_2$, as characterized by Schmerling,[12] is an effective and quite soluble alkylation catalyst. It is milder and in general effects isomerizations to a lesser extent than does aluminum chloride alone in aromatic hydrocarbon solutions.

Competitive benzylations of benzene and *n*-alkylbenzenes were carried out (as described in detail in the Experimental section) by treating equimolar quantities of the aromatics in nitromethane solutions. The mole ratio of combined aromatic substrate:benzyl chloride:$AlCl_3 \cdot CH_3NO_2$ was 10:1:1; thus a practically constant excess of the aromatics was maintained. Under the experimental conditions employed exclusive monoalkylation takes place. No detectable amount of dibenzylated products was found, either by gas-liquid chromatography or spectroscopic methods.

The reaction mixtures were analyzed by gas-liquid chromatography. Details of the analytical determination are given in the Experimental part. From the areas of individual peaks (obtained by the use of an electronic printing integrator), mole % figures were calculated for each product after first

---

(4) H. C. Brown and B. A. Bolto, *J. Am. Chem. Soc.*, **81**, 3320 (1959).

(5) H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959).

(6) R. H. Allen and L. D. Yats, *ibid.*, **83**, 2799 (1961).

(7) (a) J. H. Simons and H. Hart, *ibid.*, **66**, 1309 (1944); (b) **57**, 883 (1935); (c) T. M. Berry and E. E. Reid, *ibid.*, **49**, 3142 (1927).

(8) N. M. Cullinane and D. M. Leyson, *J. Chem. Soc.*, 2942 (1954).

(9) (a) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946; C. C. Price, *Chem. Revs.*, **29**, 37 (1941); (b) F. E. Condon, *J. Am. Chem. Soc.*, **71**, 3544 (1949).

(10) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953). L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

(11) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955.

(12) L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

determining relative response data following the method of Messner, Rosie and Argabright.[13]

The obtained relative reactivities of a number of *n*-alkylbenzenes over that of benzene, together with the isomer distributions of the monobenzylated products, are summarized in Table I. (All data were obtained as the average of at least three parallel determinations).

Table I

Competitive $AlCl_3 \cdot CH_3NO_2$-catalyzed Benzylation of Benzene and *n*-Alkylbenzenes with Benzyl Chloride in Nitromethane Solution at 25°

Ar	$k_{Ar}/k_{benzene}$	% alkyldiphenylmethane isomer distribution *ortho*	*meta*	*para*
Benzene	1.00			
Toluene	3.20	43.5	4.5	52.0
Ethylbenzene	2.45	42.4	5.0	52.6
n-Propylbenzene	2.22	39.6	8.1	52.3
n-Butylbenzene	2.08	39.1	8.6	52.3
o-Xylene	4.25	Only 3,4-dimethyldiphenylmethane detectable		
m-Xylene	4.64	19.8% 2,6- and 80.2% 2,4-dimethyldiphenylmethane		
p-Xylene	4.35			
Mesitylene	5.20			

As may be seen from the data of Table I, the benzylation of the investigated *n*-alkylbenzenes shows low substrate selectivity as compared with benzene. At the same time the amount of *m*-isomers formed is not increased to any significant amount (being between 4.5 and 8.6%). The *ortho:para* ratios as compared with other electrophilic aromatic substitutions (for example the previously investigated nitration of alkylbenzenes with nitronium tetrafluoroborate[14]) are low. This could be explained by the rather large steric hindrance in the *o*-positions effected by the bulky alkylating agent, $C_6H_5CH_2Cl \cdot AlCl_3 \cdot CH_3NO_2$.

The method of competitive rate determination can be used advantageously in determination of relative reactivities in very fast reactions, as present benzylations with benzyl chloride. However, it can be applied only if the observed relative rates are dependent on the aromatic substrates.[15] In order to establish whether actual competition between benzene and the alkylbenzenes investigated exists, the relative reactivity in toluene–benzene mixtures was determined changing the concentration in competitive experiments from the 1:1 ratio to 4:1 and to 1:4. The results—as summarized in Table II–show that the relative ratio remains almost unchanged if a first-order dependence on the aromatic substrate concentration is accepted.

The accuracy of the gas–liquid chromatographic analyses was checked with mixtures of known composition (made up from pure isomers of alkyldiphenylmethanes and the appropriate benzene–alkylbenzene mixtures) and was found to be within the limit of ±5.0% relative error. In the case of small amounts of 3-methyl- and 3-ethyl diphenylmethane the relative error, due to a certain trailing with the used capillary column, is high. However, even in these cases the accuracy is more than sufficient in evaluation of the results.

Table II

First-order Dependence of the $C_6H_5CH_2Cl + AlCl_3 \cdot CH_3 \cdot NO_2$ Benzylations in Aromatics

Toluene: benzene ratio	Obsd. rel. rates	Rel. rates according to first-order dependence in aromatics
1:4	0.76	3.04
2:3	2.11	3.17
1:1	3.20	3.20
3:2	4.58	3.05
4:1	14.0	3.50
	Average	3.19

Based on the observed isomer distributions it is believed that practically non-isomerizing and therefore only kinetically controlled reaction conditions were present for all of the investigated benzylations. Pure *o*- and *p*-alkyldiphenylmethanes were added to a tenfold excess of benzene which was then benzylated under our standard conditions. No isomerization was observed by gas–liquid chromatography. However, as discussed later, this in itself is not necessarily proof for non-isomerizing conditions. Also no disproportionation of the xylenes and mesitylene under the employed benzylation conditions was detectable.

Isopropyl- and *tert*-butylbenzene could not be investigated in this alkylation system, since in these cases always certain isomerization and disproportionation were observed which made the evaluation of results unreliable.

Kinetic Isotope Effect.—In previous work a small secondary, reverse kinetic isotope effect was found for electrophilic aromatic nitration[14,16] and a substantially larger direct effect for aromatic acetylation,[16] in both instances using pre-prepared stable nitronium and acylium salts as substituting agents. It was suggested that, in electrophilic aromatic substitutions involving strong electrophiles, small secondary isotope effects are to be expected, neither the size nor direction of which is to be predicted.[16,17]

No kinetic isotope effect was previously reported in aromatic Friedel–Crafts type alkylations. The observation of kinetic isotope effects in these systems are seriously hindered by generally strong hydrogen exchange taking place simultaneously with alkylation due to the acid catalysts employed.

It was of interest to see (a) whether our present or a related benzylation system enables kinetic isotope effect determinations in the absence of hydrogen exchange and (b) to determine the magnitude and direction of the kinetic isotope effect.

The previously described method of competitive rate determination in substitution of benzene–benzene-d_6 mixture[14] was again used to determine the kinetic isotope effect. Mass spectroscopy revealed a slight, but definite hydrogen–deuterium exchange

[13] A. E. Messner, D. M. Rosie and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[14] G. A. Olah, S. J. Kuhn and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

[15] M. J. S. Dewar, T. Mole and E. W. T. Warford, *J. Chem. Soc.*, 3576 (1956).

[16] G. A. Olah, S. J. Kuhn and S. H. Flood, XVIIIth Congress of the International Union of Pure and Applied Chemistry, Montreal, Canada, August, 1961; Abstract of Papers, p. 54.

[17] L. Melander, "Kinetic Isotope Effects," Roland Press, New York, N. Y., 1960, p. 112.

using $AlCl_3 \cdot CH_3NO_2$ as catalyst in benzylations of C_6D_6 with benzyl chloride. It was therefore necessary to find a related benzylation system free of hydrogen exchange. Using anhydrous silver tetrafluoroborate as cation-forming agent in the benzylation of benzene-d_6 with benzyl chloride in nitromethane solution, no protium–deuterium exchange was found based on mass spectroscopic analysis of the products. Ferric chloride in nitromethane solution also caused only negligible hydrogen exchange.

In order to prove that the $AgBF_4$ and $FeCl_3 \cdot CH_3NO_2$ catalyzed reactions are indeed similar in nature to the $AlCl_3 \cdot CH_3NO_2$-catalyzed benzylations, the competitive benzylations of toluene and benzene were compared. The obtained data, as summarized in Table III, show close resemblance.

TABLE III

COMPETITIVE BENZYLATION IN NITROMETHANE OF TOLUENE AND BENZENE WITH BENZYL CHLORIDE

Catalyst	Temp., °C.	k_T/k_B	Isomer distribution, % ortho	meta	para
$AlCl_3 \cdot CH_3NO_2$	25	3.20	43.5	4.5	52.0
$FeCl_3 \cdot CH_3NO_2$	25	3.24	44.5	3.7	51.8
$AgBF_4$	25	2.95	39.5	3.1	57.4

The benzyl chloride–$AgBF_4$ benzylation in nitromethane solution was used in the determination of the kinetic isotope effect in the competitive benzylation of benzene–benzene-d_6. Using mass spectroscopy to analyze the amounts of diphenylmethane and diphenylmethane-d_5 formed, a small secondary direct isotope effect was observed; $k_H : k_D = 1.12$.

The kinetic isotope effect was well reproducible when competitive benzylation, under identical conditions, of benzene–toluene and benzene-d_6–toluene mixtures were carried out. In this case gas–liquid chromatography could be used to analyze the products.

$$k_{\text{toluene}} : k_{\text{benzene}} = 3.20$$

$$k_H : k_D = 1.13$$

$$k_{\text{toluene}} : k_{\text{benzene}-d_6} = 3.62$$

The kinetic isotope effects obtained by the mass spectroscopic and gas–liquid chromatographic method thus show good agreement.

The small secondary, direct isotope effect observed can be explained by the fact that in the transition state the initial sp^2 carbon–hydrogen bond must have been changed in character at least somewhat toward that of sp^3 bonding. Owing to the low frequency of the out of plane aromatic carbon–hydrogen vibrations, it could be expected that the transition from sp^2 to sp^3 should increase the zero point energy and consequently cause a secondary alpha isotope effect with the heavy molecule reacting faster.[17] On the other hand, hyperconjugation of the carbon–hydrogen bond removed from the ring plane with the π-orbitals of the other five carbon atoms will tend to decrease the zero point energy and the two effects will cancel each other to a certain degree.[18a] Streitwieser also recently demonstrated[18b] that aromatic deuterium is electropositive relative to protium in the normal state. It is effectively electron donating relative to hydrogen, presumably because of antiharmonicity effects. In the present system, the appearance of a direct secondary isotope effect (with the heavy compound reacting slower to some extent) proves that conjugation is sufficiently strong to overcompensate the increase of zero point energy.

Discussion of Results

The observed relative reactivities of the benzylation of benzene and *n*-alkylbenzenes show good agreement with relative stabilities of complexes of alkylbenzenes with a number of π-acids such as Ag^+, HCl, Br_2, I_2, picric acid, tetracyanoethylene and also with our previously established relative nitration rates with $NO_2^+BF_4^-$.[14] However, as seen from data summarized in Table IV, no correlation with σ-complex-forming agents such as HF + BF_3 nor with known relative rates of halogenation, etc., can be established.

In comparing the present benzylation data with our previously reported $NO_2^+BF_4^-$ nitration data it must of course be kept in mind that with the present alkylation system we were unable to use a prepared, stable alkyl carbonium ion. Instead, a homogeneous alkylation system involving a reactive primary alkyl halide and a soluble catalyst ($AlCl_3 \cdot CH_3NO_2$) was used. Based on the observations of H. C. Brown[3] with a system of this kind the rate-determining alkylation step is the displacement reaction by the aromatic on the benzyl halide : catalyst complex. Thus even if the complex is highly ionized, it does not involve a free carbonium ion. This fact could account for the observed somewhat higher substrate selectivities (the toluene: benzene relative rate is 3.20 as compared with 1.67 in nitration with $NO_2^+BF_4^-$).

Although the observed relative rates are not basically different of those observed by Brown in benzylation systems,[3,4] the observed isomer distributions show a very significant difference. In all of the benzylations investigated the amount of *m*-isomer was found to be extremely low (4.5% for toluene, 5.0% for ethylbenzene, 8.1% for *m*-propylbenzene, 8.6% for *n*-butylbenzene). Consequently, as in the case of the previously reported nitrations with $NO_2^+BF_4^-$, it is meaningless to calculate partial rate factors or to apply the linear Selectivity Correlation. When an attempt was made to calculate the values for m_f from our data, they were as low as 0.43 for toluene, 0.37 for ethylbenzene, 0.54 for *n*-propylbenzene and 0.54 for *n*-butylbenzene. These values are obviously impossible for alkylbenzenes if we assume that individual positions (such as *m*-positions) are competing with one benzene position, because there is no way of explaining how one position (the *m*-position) could be considerably deactivated relative to a benzene position. However, this discrepancy can be explained, and is even to be expected, if we assume that oriented π-complex formation and not σ-complex formation is involved in the main rate-determining step. In this case competition between the π-electron systems of the molecules (as benzene and toluene), involving the π-electron systems as donor entities, takes place and not competitions between individual positions. The observed relative rates of benzylations point to such a correla-

---

(18) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958); (b) H. S. Klein and A. Streitwieser, Jr., *Chemistry & Industry*, 180 (1961).

TABLE IV

COMPARISON OF RELATIVE STABILITIES OF COMPLEXES OF ALKYLBENZENES (p-XYLENE = 1) WITH BENZYLATION RATES

Benzene ring substituents	Ag^+[a]	HCl[b]	Br_2[c]	I_2[d]	Picric[e] acid	$C_2(CN)_4$[f]	NO_2^+-BF_4^-[g] nitration	C_6H_5-CH_2Cl + $AlCl_3 \cdot CH_3$-NO_2[h] benzyln. rate	HF + BF_3[i]	Halogenation[b] rate
H	0.98	0.61	0.46	0.48	0.70	0.26	0.51	0.23		0.0005
CH_3	1.04	0.92	0.64	0.52	.84	0.49	.85	.74	0.01	.157
C_2H_5	0.86	1.06			.74		.82	.56		.13
n-C_3H_7					.98		.74	.51		
n-C_4H_9					.57		.71	.48		
o-$(CH_3)_2$	1.26	1.13	1.01	0.87	1.03	0.91	.89	.98	2.0	2.1
m-$(CH_3)_2$	1.19	1.26	0.96	1.00	0.98	0.79	.84	1.06	20.0	200.0
p-$(CH_3)_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1,3,5-$(CH_3)_3$	0.70	1.59		2.65	1.12	2.22	1.38	1.20	2800.0	80000.0

[a] N. Ogimuchi, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **78**, 2210 (1956); L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954). [b] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **71**, 3573 (1949); **74**, 3570 (1952). [c] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950). [d] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952). [e] H. D. Anderson and D. L. Hammick, *J. Chem. Soc.*, 1089 (1950). [f] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2779 (1958). [g] G. A. Olah, S. J. Kuhn and S. H. Flood, *ibid.*, **83**, 4571 (1961). [h] Present work. [i] D. A. McCauley and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951).

tion. These results thus provide support to Dewar's[19] original suggestion that π-complexes play an important role in electrophilic aromatic substitutions, even to the extent of involvement in the rate-determining step.

The potential energy diagram of the reaction, as visualized by us previously for the similar case of nitration with NO_2^+,[14] shows the main maximum (π-aromatic transition state) closely followed by the π-complex (which of course must be a minimum on the reaction path). The maximum corresponding to the π-σ transition state represents the step in which the oriented π-complex (which has involved the aromatic π-sextet as a donor entity, however, oriented in the direction of highest electron density in a substituted benzene) stabilizes to certain positions, giving the observed orientation pattern. This maximum compared with that of the primary π-complex formation, must be lower, thus eliminating reversibility or return of the once localized reagent. Whether the reaction path then goes down really to the bottom of the valley (σ-complex) or by-passes it by some type of "tunneling" is basically irrelevant concerning the directing effect. The proton elimination side of the reaction path can be interpreted similarly, the difference in the activation energy maxima being determined by the size of the kinetic isotope effect observed.

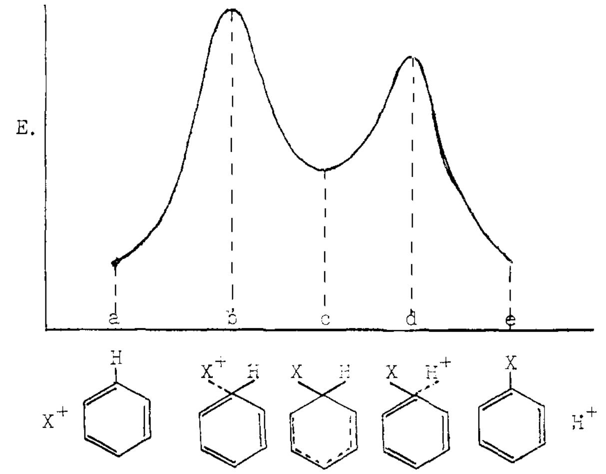


Fig. 1.

At the present time we would like to elaborate further our view of the nature of the transition state of electrophilic aromatic substitutions involving a strong electrophilic reagent (NO_2^+, incipient alkyl or aralkyl carbonium ion).

We feel that formalistic division of the reaction path into activation energy maxima leading to separate π- and σ-complexes is indeed not necessary, may frequently be confusing and distract from a better understanding of the reaction.

As Dewar[20] suggested, the actual transition state could be interpreted as a type of intermediate between the isolated molecule and reagent X^+ and the Wheland intermediate (σ-complex in H. C. Brown's terminology). This intermediate transition state can be formulated as an oriented type of π-complex (as suggested by us previously).[14] The implied energy variations along the reaction path can then be shown diagrammatically as in Fig. 1. The ordinate of the graph represents the total energy of the system. The π-electron energy would be still a maximum in the state "c." After state "b" the increase in stability due to bond formation with the reagent could more than compensate for the increase in π-electron energy.

It has been shown by Dewar[20] that the free energies of activation for electrophilic substitution in a series of aromatic hydrocarbons are linearly proportional to the atom localization energies of the most reactive position in the hydrocarbon and that the relative free energies of substitution in the various positions of a polycyclic aromatic nucleus give a similar correlation with the atom localization energy values of these positions. The atom localization energy of a given position in an aromatic hydrocarbon, which is the difference in π-electron energy between the hydrocarbon (*e.g.*, benzene) and the corresponding Wheland intermediate[21] (state "c") or benzenonium ion, is obtained[22] in

---

(19) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949, p. 168.

(20) M. J. S. Dewar, T. Mole and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); M. J. S. Dewar and T. Mole, *ibid.*, 342 (1957).

(21) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

terms of the empirical carbon–carbon resonance integral (β) which has a value of about 20 kcal./mole in the Hückel approximation[23] of the resonance energies of the aromatic hydrocarbons. (As the benzenonium ion type intermediate itself is a highly conjugated system with substantial resonance stabilization, only a part of the over-all resonance energy of the aromatic is needed to reach this stage).

If the transition state has the same general configuration for various electrophilic reactions, β will not be the true resonance integral but the numerically smaller quantity ($\beta - \beta_t^*$); moreover, this will vary with the reagent. Now β_t^* should be numerically great, and ($\beta - \beta_t^*$) numerically smaller, the more reactive the reagent. This relation holds in practice[20,24] and can be used to account for the empirical rule that the selectivity of attacking reagent is smaller the greater their reactivity.

The apparent β-values for the various reaction series increase with the selectivity of the attacking reagent for substitution at the most reactive position in a given aromatic compound from which it may be supposed that the transition state for substitution resembles more nearly the Wheland intermediate, the greater the selectivity of the attacking reagent. On the other hand, the more powerful the substituting reagent (which the incipient benzyl cation certainly is in the present work), the less selective the substitution becomes. The transition state comes then much closer to the structure "b" than to "c," which was found in some cases to be actually a stable, isolable intermediate of the benzenonium ion type and not an activated state.[25] Thus, in an extreme case, the localization energies could be interpreted for localized π-complex type of activated state and not for a Wheland or σ-complex type intermediate. This would mean numerical values for β in order of 5–10 kcal./mole instead of the $\sim$20 kcal./mole expected for a Wheland intermediate state and is in agreement with the observed numerical values.

Since the exact position of the transition state "b" depends on the reagent[20], β_x corresponding to the change of π-electron energy between "a" and "b" will be dependent on the attacking reagent too. This argument suggests that the nearer the observed value of β_x is to the theoretical value of β (~ -20 kcal./mole) the nearer the actual transition state is to the theoretical Wheland model (form "c"). On this basis the transition state for chlorination ($\beta_x = -12$ kcal./mole) is nearer to the Wheland model (σ-complex state "c") then that for nitration ($\beta_x = -6$ kcal./mole)[26] and it is suggested that corresponding apparent β_x-values for alkylations must be considerable lower than those for acylations. Thus alkylation resembles nitration, and acylation resembles chlorination.[27]

The discussion of effect of reagent activity on selectivity in our interpretations means primarily substrate and *not* necessarily positional selectivity. If the rate-determining transition state is in nature an oriented π-complex structure, we suggest that low substrate selectivity is entirely possible with maintaining usual *ortho-para* directing effects (high positional selectivity).

The question of whether or not there is a nonisolable intermediate of lower energy is trivial, since the real objective is to obtain information concerning the configuration of the transition state of the reaction irrespective of precisely what that step may be.

Although in the classical chemical sense, the intermediate is looked upon as a very unstable particle (the concept of chemical stability depending on whether or not a chemical compound can be isolated or detected by chemical means), it is stable according to thermodynamic definition because it corresponds to an energy minimum. It is thus an intermediate proper and not a transition state.

Considering the nature of the main rate-determining step for our present benzylations, it must be interpreted as the displacement step by the aromatic substrate on the benzyl chloride–Lewis acid catalyst system (as established by Brown) but leading to an oriented π-complex type, rather than to a σ-complex type activated state.

$$C_6H_5CH_2Cl + AlCl_3 \rightleftharpoons C_6H_5CH_2Cl{:}AlCl_3$$

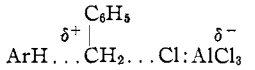
$$ArH + C_6H_5CH_2Cl{:}AlCl_3 \rightleftharpoons [ArH\ldots CH_2{}^+C_6H_5]AlCl_4{}^-$$

$$[ArH\ldots \overset{+}{C}H_2C_6H_5]AlCl_4{}^- \rightleftharpoons$$

$$[H^+\ldots ArCH_2C_6H_5]AlCl_4{}^- \rightleftharpoons$$

$$\rightleftharpoons ArCH_2C_6H_5 + HCl + AlCl_3$$

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



$$ArH\overset{\delta^+}{\ldots}\underset{}{\overset{C_6H_5}{\overset{|}{C}}}H_2\ldots \overset{\delta^-}{Cl{:}AlCl_3}$$

In this mechanism, the first step should be written either as an exchange between the nitromethane–aluminum chloride complex and the benzyl chloride

$$C_6H_5CH_2Cl + CH_3NO_2{:}AlCl_3 \rightleftharpoons C_6H_5CH_2Cl{:}AlCl_3 + CH_3NO_2$$

or even more plausibly as a ternary complex, in which the aluminum chloride forms an intermediate transition complex involving both nitromethane and benzyl chloride.

$$C_6H_5\overset{\delta^+}{C}H_2Cl\cdot\!-\!-\!\rightarrow \overset{\delta^-}{A}lCl_3 \leftarrow\!-\!-\overset{\delta^+}{O_2}NCH_3$$

In the present investigation, owing to the very fast nature of the reactions, no absolute rate determinations were attempted and first-order dependence on

---

(22) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans Faraday Soc.*, **47**, 553 (1951).

(23) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 240.

(24) K. L. McEwan and H. C. Longuet-Higgins, *J. Chem. Phys.*, **24**, 771 (1956).

(25) G. A. Olah, *et al.*, *Nature*, **178**, 694, 1344 (1956); *J. Am. Chem. Soc.*, **80**, 6535, 6540, 6541 (1958); Abstracts of Papers 138th A.C.S. Meeting, New York, N. Y., 1960, p. 3p; W. von E. Doering, M. Saunders, H. C. Baynton, E. F. Wodley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(26) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworth Scientific Publications, London, 1959, pp. 224.

(27) No significance should be given to the exact numerical values, since they would be increased by a factor of approximately two by the more exact method of calculating the localization energy of σ-complexes. The figure of -20 kcal./mole for β is also equally approximate.

the aromatic substrates were established from concentration variations in competitive rate measurements. There is, therefore, no direct proof that the reactions should also be of first order in benzyl halide and catalyst, *e.g.*, that the reactions occur by way of concerted termolecular displacement as observed by Brown, or by a more predominant preliminary ionization to carbonium ion (although complete ionization may not necessarily occur).

The difference in isomer distributions of the present benzylation system (involving oriented π-complex type of activated state formation as the main rate-determining step) over benzylations investigated by Brown and co-workers could be accounted for by the fact that our benzylation systems seem to be free of any significant isomerizations, whereas we suggest that the isomer distributions reported in previous work were those already effected by thermodynamically controlled isomerizations. If a benzylation reaction (or for that matter any other alkylation) goes through an activated state corresponding to σ-complex in nature in the rate-determining step, it is questionable that alkylation exclusive of isomerization is possible, because the latter must have an identical intermediate state. However, if the alkylation goes through an oriented π-complex type activated state as the main rate-determining step, then alkylation is possible without concurrent isomerization.

This question has theoretical interest as to whether high *m*-dialkylbenzene isomer ratios observed in many aromatic alkylations were really due to kinetically controlled direct alkylation or to thermodynamically controlled concurrent or consecutive isomerization.

Consecutive isomerization, caused either by the catalyst itself or by the conjugate acid formed by the proton elimination and interaction with the catalyst, could seriously affect isomer ratios in all alkylation reactions. Therefore, it is of predominant importance to establish whether an alkylation system is free of conditions causing consecutive isomerization. It is believed that in our present benzylation system the used donor solvent (nitromethane) complexes with the catalyst and the formed conjugated acid to a sufficient degree to inactivate it for ring protonation (σ-complex formation) and subsequent isomerization. This suggestion is supported by the fact that only a slight protium–deuterium exchange was observed in benzylation of benzene-d_6. In the absence of a suitable proton acceptor solvent (as was the case in previously reported benzylation work using only excess of the aromatics as solvent) secondary isomerizations take place much more easily. Thus in view of the experimental results it is difficult to believe that the isomer ratios were obtained under non-isomerizing conditions.

The proof of non-isomerizing conditions prevailing for alkylations as based on alkylation of a pure *o*- or *p*-dialkylbenzene isomer without observing simultaneous isomerization giving rise to the *m*-isomer[10,11,28] or alkylation of excess aromatic (*e.g.*, benzene), in the presence of smaller amounts of pure *o*- or *p*-dialkylbenzene isomers and finding no *m*-isomer formed (as also done in present investigations) is not entirely convincing. It is possible to imagine that: (a) Alkylation of the pure dialkyl isomer to trialkyl products can take place under non-isomerizing conditions; but this does not mean that in another alkylation system, *e.g.*, which leads to the dialkylbenzenes, the same conditions are fulfilled because the intermediate activated states involved are not identical. (b) Since alkylations are first order in aromatic substrate, excess benzene could be alkylated without a small amount of added pure isomers being affected even if the reaction involved a σ-complex type mechanism suitable to cause isomerization. The dialkylbenzene isomers actually undergo isomerization only if they are first transformed to a σ-complex type activated state in which a proton is attached to a carbon atom carrying an alkyl group. This could happen in the course of a concurrent alkylation taking place involving a σ-complex type rate-determining activated state, but not necessarily, if excess aromatic is alkylated which may leave the substantial part of the isomer, present in small concentration, intact. Thus negative results do not constitute definite proof that the parent alkylations are taking place under non-isomerizing conditions. Even in the case of the observed low *m*-isomer ratios in present work it can not be ruled out that some isomerization was involved, but the predominant *ortho–para* directing effect of alkyl groups in directing the entering benzyl groups is unquestionable, even in a low substrate selectivity reaction.

Our present benzylation system is the first reported example of a Friedel–Crafts type alkylation where low substrate selectivity was observed with predominant *ortho–para* directing effect and without any anomalously large amount of *m*-isomer. The main difference between the present work and previously investigations is due, in our opinion, to the fact that we were able to carry out our investigations under predominantly kinetically controlled conditions with possibly very little thermodynamically controlled concurrent isomerization.

No generalization of these results to other alkylation systems is presently attempted. It is our opinion that any generalization at the present state of knowledge is quite premature and any conclusion to be derived should be carefully confined to data obtained from specific investigated systems. A number of other alkylation systems are being investigated in our laboratory and data will be reported in forthcoming papers. Alkylations of aromatics with alkyl halides, including isopropylations and *t*-butylations, were achieved showing similar patterns to present work. It is, however, essential in any of these investigations to first establish well whether it is possible to investigate the kinetically controlled direct alkylation without interference of thermodynamically controlled secondary isomerization. High *m*-isomer ratios very frequently observed in Friedel–Crafts alkylations cannot be interpreted from a kinetic point of view when working simultaneously under thermodynamically controlled isomerizing conditions. These conditions seem to be general and difficult to avoid in most Friedel–Crafts alkylation systems.

---

[28] F. E. Condon, *J. Am. Chem. Soc.*, **71**, 3544 (1949).

Experimental

Benzene, alkylbenzenes, benzyl chloride and nitromethane used were commercial products of highest available purity. They were further purified by fractionation on an Aldershaw column rated at 50 theoretical plates. Monoalkyldiphenylmethane isomers were prepared in this Laboratory from the corresponding alkylbenzyl chlorides. The purity of the reference materials was checked by gas-liquid chromatography and infrared spectra.

$AlCl_3$ was resublimed Fisher certified reagent.

General Procedure for Competitive Benzylation.—Benzene (0.25 mole) and 0.25 mole of alkylbenzene were dissolved in 30 g. of nitromethane and 0.05 mole of $AlCl_3$ dissolved in 20 g. of nitromethane was added into this solution. The reaction flask was placed into a constant temperature bath (25°) and 0.05 mole of benzyl chloride dissolved in 20 g. of nitromethane was added dropwise into the vigorously stirred solution. The reaction time was generally 15 minutes. After the addition of the benzyl chloride the mixture was stirred for another 5 minutes, then it was washed with 100 ml. of 5% HCl–water solution, then twice with 50 ml. of water, dried over $CaCl_2$ and a small amount of K_2CO_3 and analyzed by gas-liquid chromatography.

Analytical Procedure.—The analyses were carried out by gas-liquid chromatography using a Perkin-Elmer model 154-C vapor Fractometer. Separations of methyl- and ethyldiphenylmethanes were done on a Perkin-Elmer model 154-D vapor Fractometer employing a Golay column (polypropylene glycol coating) and hydrogen flame ionization detector.

In the model 154-C vapor fractometer a 4-meter by 0.25 inch stainless steel packed column of polypropylene glycol (Ucon LB550-X) on diatomaceous earth (30% w./w.) was used with a thermistor thermal conductivity cell detector. The column temperature was 196° for all determinations. Hydrogen flowing at 60 ml. per minute was used as carrier gas. Sample sizes of 100 μml. were generally injected. Peak areas were determined with a Perkin-Elmer model 194 electron printing integrator. Relative response data were determined by running solutions of the respective alkyl-diphenylmethane isomers with diphenylmethane in benzene in approximately a 1/1/10 ratio. The retention times observed are tabulated.

The isomeric methyldiphenylmethanes and ethyldiphenylmethanes were not separable on the packed column. For the determination of these isomers a 150′ Golay capillary column (Perkin-Elmer "R-polypropylene glycol") with a hydrogen flame ionization detector was used. For the methyldiphenylmethane isomer separation, a column temperature of 100° and a helium carrier gas pressure of 30 p.s.i.g. were employed; for the ethyldiphenylmethanes, 125° and 25 p.s.i.

RETENTION TIMES OF ALKYLDIPHENYLMETHANES AT 195° ON PACKED COLUMN

Diphenylmethane	Retention time, min.	Diphenylmethane	Retention time, min.
Unsubstd.	35	3-*n*-Butyl-	103
2-Methyl-	51	4-*n*-Butyl-	125
4-Methyl-	54	3,4-Dimethyl-	66
2-Ethyl	58	2,6-Dimethyl-	53
4-Ethyl-	67	2,4-Dimethyl-	60
2-*n*-Propyl-	63	2,5-Dimethyl-	52
3-*n*-Propyl-	69	2,4,6-Trimethyl-	100
4-*n*-Propyl	80		
2-*n*-Butyl-	90		

RETENTION TIMES OF ISOMERIC METHYLDIPHENYLMETHANES AND ETHYLDIPHENYLMETHANES ON GOLAY COLUMN

Alkyldiphenylmethane	Retention time, min.
2-Methyl-	60
3-Methyl-	62
4-Methyl-	65
2-Ethyl-	23
3-Ethyl-	24
4-Ethyl-	27

Determination of Kinetic Isotope Effect.—A mixture of 0.1 mole of benzene and 0.1 mole of benzene-d_6 was benzylated in nitromethane solution at 25° in the same manner as were the other competitive benzylations carried out. The resulting mixture was washed, dried and analyzed by mass spectroscopy.

Competitive benzylation of toluene (0.1 mole) and benzene-d_6 (0.1 mole) in nitromethane solution at 25° was carried out similarly, but products were analyzed by gas-liquid chromatography.

Acknowledgment.—The authors are indebted to R. S. Gohlke (Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Mich.) for the mass spectroscopic analyses.

[CONTRIBUTION NO. 55 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

Aromatic Substitution. XI.[1] The $AlCl_3CH_3NO_2$-Catalyzed Benzylation of Halobenzenes with Benzyl Chloride in Nitromethane Solution

BY GEORGE A. OLAH, STEPHEN J. KUHN AND SYLVIA H. FLOOD

RECEIVED OCTOBER 25, 1961

Competitive $AlCl_3 \cdot CH_3NO_2$-catalyzed benzylation of benzene and halobenzene with benzyl chloride in homogeneous nitromethane solution was investigated. Relative rates and isomer distributions were determined by a gas-liquid chromatographic analytical method using a Golay type capillary column and a hydrogen flame ionization detector. The observed relative rates, the reactions being first order in aromatics show good correlation with relative π-complex stabilities of the halobenzenes. The mechanism of the reactions is discussed based on the obtained experimental data.

Introduction

In the previous paper of this series[1] the $AlCl_3$-CH_3NO_2-catalyzed benzylation of alkylbenzenes with benzyl chloride in nitromethane solution was investigated. This work has now been extended to a similar investigation of the benzylation of halobenzenes.

Results

Competitive benzylations of benzene and halobenzenes were carried out under identical conditions as described previously in the case of alkylbenzenes. All benzylations were carried out in nitromethane solutions at +25°. Under the employed experimental conditions only monobenzylation takes place. No di- or higher benzylated products were detectable in the reaction mixtures either by gas-liquid chromatographic or spectroscopic methods. The reaction mixtures were analyzed by a gas-liquid chromatographic method, using a Golay-type capillary column and a hydrogen flame ionization detector. From the areas of individual peaks (obtained by the use of an electronic printing

---

[1] Part X, *J. Am. Chem. Soc.*, **84**, 1688 (1962).