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Studies of Diarylalkanes. V.[*1, 1)] The Benzylation of Benzene and Chlorobenzene with Benzyl or *p*-Chlorobenzyl Chloride under the Influence of Various Catalysts

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The benzylation of benzene and chlorobenzene with benzyl or *p*-chlorobenzyl chloride under the influence of various catalysts has been carried out in order to elucidate the relation between the cleavage reaction of the DPM and the Friedel-Crafts benzylation. In the aluminum chloride- or gallium chloride-catalyzed benzylation, the compositions of the equilibrium mixture are similar to those of the cleavage reaction. It has been suggested that, in the presence of such catalysts, the DPM formed at an initial stage is cleft with the catalyst, and that the same equilibrium relationship as has been postulated in the cleavage reaction is established. On the other hand, in the aluminum chloride-, gallium chloride-nitro compound complex or in indium chloride, which does not exhibit the ability to cleave the DPM, both the products and the isomer distributions are different. It has been estiablished that the isomer distributions in the benzylation are affected by the reactivity of the reactive species as well as by the catalytic ability to cleave the DPM. It has also been found that, under the influence of a strong catalyst such as the aluminum chloride - nitromethane complex, the relative reactivity of *p*-chlorobenzyl chloride on benzene is equal to that of benzyl chloride, while the reactivity of the former is about half that of the latter in the presence of such a weak catalyst as indium chloride.

During the course of the study of the cleavage reaction of diarylmethanes under the influence of aluminum chloride, an investigation was carried out in order to elucidate the relation between the cleavage reaction and the Friedel-Crafts benzylation.

In a previous work[1)] dealing with the cleavage of diphenylmethane (DPM), chloro- (Cl-DPM)

[*1] Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964, and at the 15th Symposium of the Organic Reaction Mechanism, Nagoya, October, 1964.

1) Part IV: O. Tsuge and M. Tashiro, This Bulletin, **40**, 115 (1967).

Table 1. The competitive benzylation of benzene and chlorobenzene with benzyl chloride

Time, min	Product, mol%				Isomer of Cl-DPM, %		
	DPM	Cl-DPM	Cl_2-DPM	Anthracene	ortho	meta	para
2	55.9	39.1	5.0	—	48.1	trace	51.9
5	48.3	43.9	7.8	—	36.9	26.2	36.9
10	44.2	49.2	5.3	1.3	23.4	39.4	37.2
15	37.8	52.2	8.3	1.7	21.1	50.9	28.0
20	37.0	53.7	8.1	1.2	16.9	54.6	28.5
30	38.2	50.7	8.4	2.7	15.1	56.6	28.3
40	38.0	51.2	6.8	4.0	21.4	50.0	28.6
50	38.9	47.8	9.0	4.3	19.9	54.1	26.0

Table 2. The competitive benzylation of benzene and chlorobenzene with *p*-chlorobenzyl chloride

Time, min	Product, mol%				Isomer of Cl-DPM, %		
	DPM	Cl-DPM	Cl_2-DPM	Anthracene	ortho	meta	para
2	18.0	68.2	9.8	4.0	38.3	—	61.7
7	33.8	58.8	6.0	1.4	51.6	—	48.4
12	45.3	45.5	8.0	1.2	38.0	22.8	39.2
17	46.4	46.4	5.8	1.4	34.4	28.8	36.8
22	42.7	47.7	7.5	2.1	32.4	35.2	32.4
27	40.1	54.0	4.0	1.9	32.1	41.1	26.8
32	39.7	50.9	7.7	1.8	30.3	43.0	26.7
37	39.5	51.8	7.0	1.7	30.9	43.9	25.2
47	38.2	50.7	9.3	1.8	31.7	41.5	26.8

and dichlorodiphenylmethane (Cl_2-DPM) in a mixture of benzene and chlorobenzene, it was shown that a first-order dependence on the aromatic substrate concentration exists, and that an equilibrium relationship consisting of four systems is established among the products. It was also suggested that the cleavage reaction is closely connected with the Friedel-Crafts benzylation.

Only a little information has been available regarding the benzylation of chlorobenzene with benzyl chloride or that of benzene with chlorobenzyl chloride. Koike and Okawa(2) reported that, in the benzylation of chlorobenzene, while Cl-DPM consisting of 57% *o*-, 32% *m*-, and 11% *p*-isomer was obtained in a yield of 43.8% under the influence of aluminum chloride, the yield of Cl-DPM was 9.5%; in it the isomer distribution was 84% *o*- and 16% *p*-isomer in the presence of zinc chloride. It was also observed by Olah and his co-workers(3) that the Cl-DPM formed by the aluminum chloride - nitromethane catalyzed benzylation of chlorobenzene consisted of 33.0% *o*-, 0.6% *m*-, and 66.4% *p*-isomer. However, no relation between the benzylation and the cleavage reaction has ever been taken into consideration.

In the present work, the benzylation of benzene and of chlorobenzene with benzyl or *p*-chlorobenzyl chloride under the influence of various catalysts was studied in order to obtain clearer information concerning the relation between the benzylation and the cleavage reaction.

Experimental

Materials. Benzyl chloride (bp 179°C), *p*-chlorobenzyl chloride (bp 70.5—71°C/20 mmHg), benzene (bp 80°C), chlorobenzene (bp 132°C), nitromethane (bp 102°C), nitroethane (bp 114°C), 1-nitropropane (bp 132°C), 2-nitropropane (bp 120°C), and nitrobenzene (bp 211°C) were each purified by distillation.

Aluminum chloride, ferric chloride and indium chloride were purified by sublimation just before use, and titanium tetrachloride (bp 137°C) was distilled in the presence of copper powder. The other catalysts were used in commercial grades.

The diphenylmethanes used as standard samples were prepared according to the reported method and were purified by fractional distillation and/or recrystallization. DPM:(4) bp 140—141°C/5 mmHg; mp 25°C; retention time (hereafter referred to as R. T.),(5) 4.6 min. 2-Cl-DPM:(6) bp 127—128°C/1.5 mmHg; n_D^{25} 1.5915; R. T., 6.1 min. 3-Cl-DPM:(6) bp 163—166°C/12 mmHg; n_D^{25} 1.5892; R. T., 7.0 min. 4-Cl-DPM:(6) bp 130—135°C/3 mmHg; n_D^{25} 1.5885; R. T., 7.9 min.

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2) E. Koike and K. Okawa, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 83 (1954).

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

4) "Organic Syntheses," Coll. Vol. II, p. 232 (1948).

5) Column: 30% High-vacuum silicon grease; Column temperature: 235°C; Carrier gas: Hydrogen, 22 m*l*/min.

6) J. Blackwell and W. H. Hickinbotton, *J. Chem. Soc.*, **1961**, 1405.

2, 4′-Cl$_2$-DPM:6) bp 183—185°C/11 mmHg; n_D^{25} 1.5996; R. T., 13.9 min. 4, 4′-Cl$_2$-DPM:6) bp 147—154°C/3 mmHg; mp 56—57°C; R. T., 14.8 min.

Analytical Procedure. The products were analyzed by gas chromatography using a Shimadzu Gas Chromatograph, GC-IB. From the areas of individual peaks, the mol% figures were calculated for each product after determining the relative response data by the internal standard method. In some cases, nitrobenzene was used as the internal standard substance.

The data in the tables are given as the average of at least three parallel determinations. In all cases, reactants were used in these proportions: the benzyl chloride (1 mol), the benzene and/or the chlorobenzene (20 mol), and the catalyst (0.1 mol). The typical procedures were as follows.

The Competitive Benzylation of Benzene and Chlorobenzene under the Influence of Aluminum Chloride. *i) With Benzyl Chloride.* After 13.11 g (104 mmol) of benzyl chloride had been added to a mixture of 78.0 g (999 mmol) of benzene, 112.0 g (995 mmol) of chlorobenzene, and 1.59 g (12 mmol) of aluminum chloride at 40°C, 1-m*l* aliquots of the mixture were withdrawn from time to time by means of a pipet and were quenched with dilute hydrochloric acid. After the quenched products had been well extracted with ether, the ether solution was washed with water, dried over sodium sulfate, and then analyzed by gas chromatography. The results are shown in Table 1.

ii) With p-Chlorobenzyl Chloride. The reaction of 48.0 g (615 mmol) of benzene and 69.0 g (613 mmol) of chlorobenzene with 9.86 g (49 mmol) of *p*-chlorobenzyl chloride in the presence of 0.48 g (4 mmol) of aluminum chloride was carried out at 40°C; the products were then determined by a treatment similar to that described above. The results are shown in Table 2.

The Benzylation of Benzene with *p*-Chlorobenzyl Chloride. *i) Under the Influence of Aluminum Chloride.* To a mixture of 86.66 g (1110 mmol) of benzene and 0.49 g (4 mmol) of aluminum chloride there was added 9.33 g (46 mmol) of *p*-chlorobenzyl chloride at 40°C; the mixture was then treated with the way described above. The results are shown in Table 3.

ii) Under the Influence of Ferric Chloride. To a mixture of 17.58 g (225 mmol) of benzene and 0.2 g (1.2

TABLE 3. THE BENZYLATION OF BENZENE WITH *p*-CHLOROBENZYL CHLORIDE

Time min	Product, mol%			Isomer of Cl-DPM, %		
	Chloro-benzene	DPM	Cl-DPM	ortho	meta	para
1	0.2	2.0	98.0	—	—	100
3.3	0.5	11.8	88.2	trace	—	100
5	0.6	11.0	89.0	trace	—	100
10	2.2	68.5	31.5	no determined		
20	5.3	94.4	5.6	5.5	trace	94.5
30	4.9	95.1	4.9	24.9	33.6	41.5
42	4.4	94.9	5.1	no determined		
51	4.9	95.6	4.4	29.2	33.6	37.2
80	4.5	95.8	4.2	25.8	43.7	30.5
125	5.1	95.5	4.5	23.9	42.1	34.0
165	5.1	96.7	3.3	26.2	45.5	28.3

TABLE 4. THE EQUILIBRIUM MIXTURE IN THE COMPETITIVE BENZYLATION UNDER THE INFLUENCE OF ALUMINUM CHLORIDE a)

Bzy b)	4-Cl-Bzy b)	Product, mol% c)			Isomer of Cl-DPM, %		
		DPM	Cl-DPM	Cl$_2$-DPM	ortho	meta	para
1.0	0	37.8	50.4	8.4	22.8	53.2	24.0
0.5	0.5	38.9	53.2	7.0	28.2	50.5	21.3
0	1.0	39.7	50.1	7.8	27.7	43.6	28.7
	Calculated:	40	50	10			

a) The molar ratios of benzene, chlorobenzene, and aluminum chloride to the benzyl chloride were 10, 10 and 0.1 respectively. Reaction time : 60 min. Temperature: 40°C.

b) Bzy and 4-Cl-Bzy are represented by benzyl and *p*-chlorobenzyl chloride respectively in all the tables.

c) Anthracene was formed in 0.6, 2.1 and 2.4 mol% in the respective cases.

TABLE 5. THE EQUILIBRIUM MIXTURE IN THE COMPETITIVE BENZYLATION UNDER THE INFLUENCE OF ALUMINUM CHLORIDE - NITROMETHANE COMPLEX*

Bzy	4-Cl-Bzy	Product, mol%			Isomer of Cl-DPM, %			Isomer of Cl$_2$-DPM, %		
		DPM	Cl-DPM	Cl$_2$-DPM	ortho	meta	para	2, 4′-	3, 4′-	4, 4′-
1.0	0	80.0	20.0	—	34.0	—	66.0	—	—	—
0.5	0.5	39.2	52.3	8.5	2.0	—	98.0	32.3	—	67.7
	Calculated:	40	50	10	6.8	—	93.2	34.0	—	66.0
0	1.0		84.8	15.2			100	33.3	—	66.7
	Calculated:		80	20			100	34.0	—	66.0

* The molar ratio of benzene, chlorobenzene and the catalyst to the chloride was 10, 10 and 0.1 respectively. Reaction time; 15 min. Temperature; 40°C.

mmol) of ferric chloride there was added 2.0 g (9.86 mmol) of *p*-chlorobenzyl chloride all at once at 40°C; the reaction mixture was stirred at the same temperature for 30 min, and then the mixture was decomposed with water. The quenched products were extracted with ether, and the ether solution was dried over sodium sulfate. To the ether solution 1.0 g of nitrobenzene was added as the internal standard substance, and the solution was analyzed by gas chromatography. The results with various catalysts are summarized in Table 7.

The Competitive Benzylation of Benzene and Chlorobenzene with Benzyl Chloride under the Influence of the Aluminum Chloride - Nitromethane Complex. The reaction of 87.9 g (112.5 mmol) of benzene and 11.10 g (98.6 mmol) of chlorobenzene with 1.0 g (7.0 mmol) of benzyl chloride in the presence of the aluminum chloride-nitromethane complex (0.1 g of aluminum chloride in 1 m*l* of nitromethane) was carried out in the way described above. The products were then analyzed by gas chromatography, using nitrobenzene as the internal standard substance. The results under varying catalysts are summarized in Tables 5, 8 and 10.

TABLE 6. THE FIRST-ORDER DEPENDENCE ON THE CHLORIDE[a]

4-Cl-Bzy/Bzy[b]	Observed[b] 4-Cl-DPM/DPM	Calculated[c] 4-Cl-DPM/DPM
2.11	2.18	1.03
0.92	0.98	1.07
0.47	0.44	0.94

a) Mixtures of a definite amount of the combined chloride, 20 mol of benzene, and 0.1 mol of the catalyst per mole of the chloride were heated at 40°C for 15 min.

b) Molar ratio.

c) Molar ratio according to the first-order dependence on the chloride.

The Competitive Benzylation of Benzene with Benzyl Chloride and *p*-Chlorobenzyl Chloride. A mixture of 0.85 g (6.77 mmol) of benzyl chloride and 1.0 g (6.21 mmol) of *p*-chlorobenzyl chloride was added to a suspension of 0.20 g (0.9 mmol) of indium chloride in 16.58 g (212.2 mmol) of benzene at 40°C over a 30-min period; the reaction mixture was then treated in the way described above. The results are shown in Table 9.

Results and Discussion

The Aluminum Chloride-catalyzed Benzylation. The competitive benzylations of benzene and chlorobenzene with benzyl chloride or *p*-chlorobenzyl chloride were carried out at 40°C. The results are shown in Tables 1 and 2 respectively.

As is shown in the tables, the compositions of the equilibrium mixtures are similar to those of the cleavage of DPM, Cl-DPM or Cl_2-DPM with aluminum chloride in a mixture of benzene and chlorobenzene.[1] This suggests that the DPM formed at an initial stage is cleft with the catalyst, and that the same equilibrium relationship as has been postulated previously in the cleavage reaction[1] is also established here.

TABLE 7. THE BENZYLATION OF BENZENE WITH *p*-CHLOROBENZYL CHLORIDE UNDER THE INFLUENCE OF VARIOUS CATALYSTS

Run	Temp. °C	Time min	Catalyst	Product, mol%		Isomer of Cl-DPM, %		
				DPM	Cl-DPM	ortho	meta	para
1	95	15	$AlCl_3$	93.3	6.7	26.4	44.3	29.3
2	95	15	$AlCl_3$-$C_6H_5NO_2$	—	100	—	—	100
3	95	15	Al	1.7	98.3	trace	trace	100
4	95	15	Al-Hg	3.0	97.0	trace	trace	100
5	40	60	$GaCl_3$	92.4	7.6	27.3	50.1	22.6
6	95	15	$GaCl_3$	92.5	7.5	26.8	48.5	24.7
7	95	15	$GaCl_3$-$MeNO_2$	—	100	—	—	100
8	95	15	$GaCl_3$-$C_6H_5NO_2$	—	100	—	—	100
9	95	15	$FeCl_3$	—	100	—	—	100
10	95	15	Fe	—	100	—	—	100
11	40	60	$InCl_3$	—	37.0	—	—	100
12	95	15	$InCl_3$	—	85.7	—	—	100
13	95	15	$HgCl_2$	—	19.0	—	—	100
14	95	15	$CdCl_2$	—	10.6	—	—	100
15	95	15	$ZnCl_2$	—	4.3	—	—	100
16	95	15	$SnCl_4$	—	5.1	—	—	100
17	95	15	Zn-Hg	—	9.1	—	—	100
18	95	15	Zn	—	2.7	—	—	100
19	95	15	Mg	—	5.8	—	—	100
20	95	15	$TiCl_4$	—	3.5	—	—	100
21	95	15	$SbCl_3$	—	3.8	—	—	100

TABLE 8. THE COMPETITIVE BENZYLATION OF BENZENE AND CHLOROBENZENE WITH BENZYL CHLORIDE UNDER THE INFLUENCE OF VARIOUS CATALYSTS

Run	Temp. °C	Time min	Catalyst	Product, mol%		Isomer of Cl-DPM, %		
				DPM	Cl_2-DPM	ortho	meta	para
1	40	30	$AlCl_3$-$EtNO_2$	80.6	19.4	30.0	—	70.0
2	40	30	$AlCl_3$-*n*-$PrNO_2$	81.1	18.9	30.4	—	69.6
3	40	30	$AlCl_3$-iso$PrNO_2$	80.0	20.0	30.9	—	69.1
4	40	30	$AlCl_3$-$C_6H_5NO_2$	82.7	17.3	30.7	—	65.3
5*	40	30	$GaCl_3$	36.9	50.4	14.8	57.8	27.4
6	40	30	$GaCl_3$-$MeNO_2$	82.6	17.4	32.9	—	67.1
7	40	30	$GaCl_3$-$C_6H_5NO_2$	83.2	16.8	30.3	—	69.7
8	40	30	$FeCl_3$	84.0	16.0	32.7	—	67.3
9	40	30	$FeCl_3$-$MeNO_2$	83.3	16.7	30.0	—	70.0
10	95	15	$FeCl_3$	84.6	15.4	30.5	—	69.5
11	95	15	$InCl_3$	84·6	15.4	38.5	—	61.5
12	95	15	Al	84.6	15.4	30.5	—	69.5
13	95	15	Fe	84.0	16.0	33.6	—	66.4

* Cl_2-DPM and anthracene were formed in 9.2 and 3.5 mol% respectively.

TABLE 9. THE FIRST-ORDER DEPENDENCE ON THE CHLORIDE

4-Cl-Bzy/ Bzy[a)]	Observed[a)] 4-Cl-DPM/DPM	Calculated[b)] 4-Cl-DPM/DPM
2.11	1.04	0.49
0.92	0.43	0.47
0.47	0.22	0.47

a) Molar ratio.

b) Molar ratio according to the first-order dependence on the chloride.

TABLE 10. THE FIRST-ORDER DEPENDENCE ON THE AROMATICS[a)]

Chlorobenzene/ Benzene[b)]	Observed[b)] Cl-DPM/DPM	Calculated[c)] Cl-DPM/DPM
0.18	0.04	0.22
0.87	0.17	0.20
2.58	0.45	0.17

a) Mixtures of a definite amount of benzyl chloride, 20 mol of the combined aromatics, and 0.1 mol of the catalyst per mole of the chloride were heated at 40°C for 1 hr. (In the benzylation of benzene with benzyl chloride under these conditions, DPM was formed in about a 84% yield.)

b) Molar ratio.

c) Molar ratio according to the first-order dependence on the aromatics.

Although it has generally been accepted that the high yield of the *m*-isomer in the electrophilic substitution is due to the high reactivity, and hence the low selectivity, of the reactive species,[7] the data in the tables indicate that, even under the influence of such a strong catalyst as aluminum chloride, the normal products, *o*- and *p*-Cl-DPM, were predominantly formed at the initial stage, and that the formation of a large amount of *m*-isomer resulted only from a secondary reaction. Namely, there seems to be a close relationship between the cleavage reaction and the product distribution.

As is shown in Table 3, this theory seems to be supported by the fact that chlorobenzene was formed in almost a theoretical amount (5 mol%) and that the Cl-DPM formed was consumed, while DPM was formed in a large amount with an increase in the reaction time. Moreover, the isomer distribution of Cl-DPM was changed from pure *p*-isomer to a mixture of isomers.

It is notable that, in the aluminum chloride-catalyzed benzylation with the substituted benzyl chloride, using excess benzene as solvent, the expected DPM is not always obtained, but the undesirable DPM is formed as the main product during a long reaction time.

The equilibrium mixtures in the competitive reactions of benzene and chlorobenzene with benzyl chloride and/or *p*-chlorobenzyl chloride, under the influence of aluminum chloride alone or of an aluminum chloride - nitromethane complex, are shown in Tables 4 and 5 respectively.

In the case of aluminum chloride alone, as is shown in Table 4, neither the kinds of products nor the isomer distribution of Cl-DPM was very much affected by the change in the molar ratio of benzyl chloride and *p*-chlorobenzyl chloride. Although many kinds of Cl_2-DPM isomers were formed, they could not be identified.

In the aluminum chloride - nitromethane-catalyzed benzylations (Table 5), however, both the

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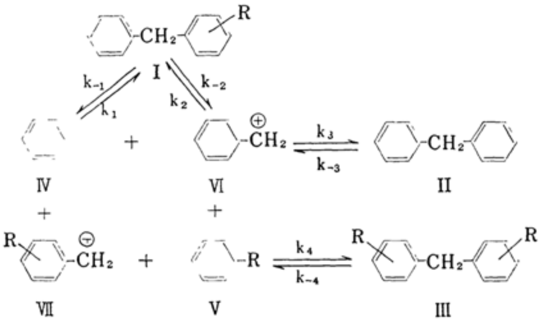
[7] H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

products and the isomer distributions were different.

As has been mentioned above, the following equilibrium relationship is established in the aluminum chloride-catalyzed benzylation:



where k_1, k_2, k_3 and k_4, and k_{-1}, k_{-2}, k_{-3} and k_{-4} are the rate constants of the formation and of the consumption of the corresponding DPM in the respective systems.

On the other hand, in order to establish whether actual competition between benzyl chloride and *p*-chlorobenzyl chloride exists in the presence of the aluminum chloride - nitromethane complex, the relative reactivity of the chlorides was determined by the changing the concentration of the chlorides in the competitive reaction against benzene (Table 6).

As is shown in Table 6, it is indicated that the relative rate has a first-order dependence on both chlorides, and that the apparent reactivities of the chlorides on benzene are equal to each other.

Since, in the complex-catalyzed benzylation, the cleavage reaction did not take place, and since the reactivity of benzyl chloride is equal to that of *p*-chlorobenzyl chloride, as Tables 5 and 6 show, the rate constants of the consumption are zero and k_2/k_3 is equal to k_4/k_1. From the data of the first column in Table 5, k_2/k_3 is found to be 0.25.

Consequently, the calculated values for the second column may be given as follows: the molar ratio among DPM, Cl-DPM and Cl_2-DPM is 1.00, 1.25 and 0.25; that is, 40, 50 and 10 mol% respectively. Under the conditions of the last column, k_2 and k_3 are also zero. Therefore, the molar ratios between Cl-DPM and Cl_2-DPM are 1.00 and 0.25, that is, 80 and 20 mol%, in the respective cases.

The isomer distributions of Cl-DPM and Cl_2-DPM are also calculated on the basis of the data in the first column in Table 5. The calculated values are in agreement with the respective observed values. These findings will be detailed in the next paper.

The Effect of the Catalyst on the Benzylation. It seemed of interest to investigate whether any catalyst exhibits the ability to cleave the DPM formed in the benzylation. The benzylations of benzene with *p*-chlorobenzyl chloride and the competitive benzylations of benzene and chlorobenzene with benzyl chloride were therefore carried out under the influence of various catalysts. The results are summarized in Tables 7 and 8.

As is shown in the tables, gallium chloride exhibited an ability comparable to that of aluminum chloride. It has been also found that aluminum metal and aluminum amalgam exhibited an ability somewhat similar to that of aluminum chloride, but their ability was very weak. However, the cleavage reaction did not take place in the benzylations under the influence of the other catalysts cited in the tables. Under the influence of the aluminum chloride-, gallium chloride - nitro compound complex, ferric chloride, iron, or indium chloride, the expected *p*-Cl-DPM is obtained in a good yield.

The Competitive Benzylation under the Influence of Indium Chloride. As is shown in Table 7, indium chloride did not cause the cleavage of the DPM, and its catalytic activity was weaker than that of the aluminum chloride-nitro compound. In the same manner as in the case of the aluminum chloride - nitromethane complex (Table 6), the relative reactivities of both benzyl chloride and *p*-chlorobenzyl chloride were determined using the competitive benzylation of benzene under the influence of indium chloride. The results are shown in Table 9.

As Table 9 shows, the results indicate that the molar ratio of 4-Cl-DPM to DPM remains almost unchanged if the first-order dependence on the chloride is accepted.

It is also suggested that, under the influence of indium chloride, the relative reactivity of *p*-chlorobenzyl chloride on benzene is about half that of benzyl chloride, although the reactivity of the former is equal to that of the latter in the presence of aluminum chloride - nitromethane.

Furthermore, in order to establish whether or not there is actual competition between benzene and chlorobenzene in the competitive indium chloride-catalyzed benzylation, the reaction was carried out with a different concentration of aromatics. The results are shown in Table 10.

As may be seen in Table 10, the molar ratio of Cl-DPM to DPM remains almost unchanged if the first-order dependence on the aromatics is accepted. The relative reactivity of chlorobenzene against benzene is about 0.2.

Consequently, it is revealed that the benzylation under the influence of indium chloride is of the first order in an aromatic component and in the benzyl chloride respectively.