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Studies of Diarylalkanes. VI.[1,2] The Cleavage of Diphenylmethanes and the Friedel-Crafts Benzylation

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The cleavage reaction of DPM and Me-DPM, and the benzylation of toluene, have been carried out under various conditions. On the basis of the results of this series, the correlations with the cleavage reaction of the DPM and with the Friedel-Crafts benzylation have been inclusively discussed. Furthermore, the mechanism of the isomerization of mono-substituted DPM under the influence of aluminum chloride has been suggested.

During the course of a study of correlations with the cleavage reaction of the DPM[*1] and the Friedel-Crafts benzylation, we have discussed the cleavage reaction of the DPM in a large amount of aromatics serving as solvents,[3,4] and the benzylation of benzene and chlorobenzene under various conditions.[2]

The present paper will deal with the cleavage reaction of DPM and Me-DPM and the benzylation of toluene under various conditions; there will also be a general discussion.

Experimental

Materials. The diphenylmethanes were prepared by the reported method and were purified by fractional distillation and/or recrystallization. DPM:[5] bp 140—141°C/5 mmHg; mp 25°C; retention time, 4.6 min. 2-Me-DPM:[6] bp 162.5—163°C/29 mmHg; n_D^{25} 1.5737. 3-Me-DPM:[6] bp 161—162°C/26 mmHg; n_D^{25} 1.5698. 4-Me-DPM:[6] bp 164—165.5°C/28 mmHg; n_D^{25} 1.5661. Aluminum chloride, ferric chloride, and indium chloride were purified by sublimation just before use, while titanium tetrachloride (bp 137°C) was distilled in the presence of copper powder. The other catalysts were used in a commercial grade.

Analytical Procedure.—The products were mainly analyzed by gas chromatography using a Shimadzu Gas Chromatograph, GC-IB. The conditions for the gas chromatographic analyses were as follows: column, 30% high vacuum silicon grease; column temperature, 235°C; carrier gas, hydrogen, 22 ml/min. From the areas of the individual peaks, mol% figures were calculated for each product after the relative response data had been determined by the internal standard method.

The Me-DPM isomers were not sufficiently separated on the column, although it was possible to separate the 2-isomer from the combined 3- and 4-isomer. Therefore, the concentrations of the Me-DPM isomers were estimated by the quantitative analysis of the infrared spectra recorded from a carbon disulfide solution. The out-of-plan hydrogen deformation frequencies at 740, 780 and 790 cm^{-1} were used for the determination of 2-, 3- and 4-Me-DPM respectively. The mixture of Me-DPM isomers obtained by the reaction was collected by gas chromatography and then analyzed by the infrared spectroscopic method.

The cleavage reaction and benzylation were carried out in a procedure similar to those reported previously.[2,4]

Results and Discussion

The Cleavage of DPM and 4-Me-DPM in a Mixture of Benzene and Toluene.—Table 1 shows the products at equilibrium for the reactions of DMP and 4-Me-DMP with water-promoted aluminum chloride[4] in a mixture of benzene and toluene.

The available data reveal that an equilibrium relationship similar to that suggested in previous paper[4] is established among the products.

A General Discussion of the Cleavage Reaction. As has been mentioned in previous papers

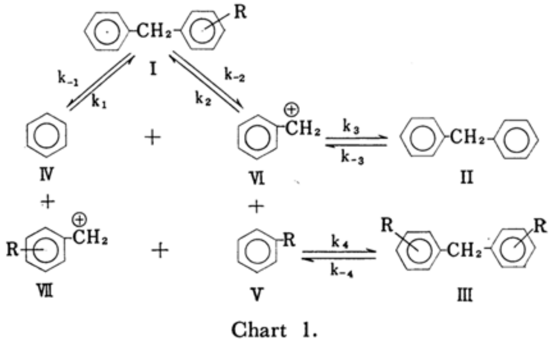

Chart 1.

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1) Presented at the General Meeting of the Kyushu District of the Pharmaceutical Society of Japan, Fukuoka, February, 1965.

[*1] Abbreviations: DPM, Me-, Me$_2$-, Cl- and Cl$_2$-DPM; Diphenylmethane, Methyl-, Dimethyl-, Chloro- and Dichlorodiphenylmethane respectively.

2) Part V: This Bulletin, **40**, 119 (1967).

3) O. Tsuge and M. Tashiro, *ibid.*, **38**, 184 (1965).

4) Part IV: *ibid.*, **40**, 115 (1967).

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

6) J. H. Lamneck, Jr., and P. H. Wise, *J. Am. Chem. Soc.*, **76**, 1104 (1954).

TABLE 1. THE PRODUCTS AT EQUILIBRIUM IN THE CLEAVAGE OF DPM AND 4-Me-DPM*

Compound	Product, mol%			Isomer of Me-DPM, %		
	DPM	Me-DPM	Me_2-DPM	ortho	meta	para
DPM	43.7	46.7	10.6	12.1	62.1	25.8
4-Me-DPM	38.8	48.8	11.6	11.9	63.6	24.5
Average:	41.3	47.8	11.1			

* DPM was reacted with water-promoted aluminum chloride (0.1 mol of aluminum chloride and 0.025 mol of water) in a mixture of benzene and toluene (each 10 mol of the DPM) at 50°C for 1 hr.

of this series, it is evident that, in the cleavage reaction of the DPM with aluminum chloride in the presence of a binary mixture of aromatics, the following equilibrium relationship is established (Chart 1):

Here, 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 consumption of the corresponding DPM respectively.

The cleavage reaction of the DPM in the presence of aromatics as solvents depends on the first order in the DPM and in the IV and V aromatics, respectively.[4)] Since it may also be assumed that, the IV and V aromatics being in excess, these concentrations remain unchanged, the concentrations of R-DPM (I), DPM (II) and R_2-DPM (III), that is [R-DPM], [DPM] and [R_2-DPM], should be given by the following equations in the respective cases:

$$[\text{R-DPM}] = k_1/k_{-1}\cdot[\text{R-Bzy}] + k_2/k_{-2}\cdot[\text{Bzy}] \quad (1)$$

$$[\text{DPM}] = k_3/k_{-3}\cdot[\text{Bzy}] \quad (2)$$

$$[\text{R}_2\text{-DPM}] = k_4/k_{-4}\cdot[\text{R-Bzy}] \quad (3)$$

where [R-Bzy] and [Bzy] are the concentrations of the benzyl cation entities, VI and VII respectively.

Hence,

$$[\text{R-DPM}]/[\text{DPM}] = k_2/k_3\cdot k_{-3}/k_{-2}+k_1/k_{-1}\cdot k_{-3}/k_3\cdot[\text{R-Bzy}]/[\text{Bzy}] \quad (4)$$

$$[\text{R}_2\text{-DPM}]/[\text{DPM}] = k_4/k_3\cdot k_{-3}/k_{-4}\cdot[\text{R-Bzy}]/[\text{Bzy}] \quad (5)$$

If we assume that i) the relative reactivity of the benzyl cation entity (VI) is equal to that of the benzyl cation entity (VII),[7)] and that ii) the rate of the cleavege of the bond between the aromatic ring with the same substituent and methylene group is equal in the DPM (I—III), in other words, that the aromatic rings in the DPM behave independently of each other in the cleavage reaction, then $k_1=k_3$ and $k_2=k_4$, and $k_{-1}=k_{-3}$, $k_{-2}=k_{-4}$ and [Bzy]=[R-Bzy].

Applying the above approximations to Eqs. (4) and (5), we obtain:

$$[\text{R-DPM}]/[\text{DPM}]=k_2/k_3\cdot k_{-1}/k_{-2}+1 \quad (6)$$

$$[\text{R}_2\text{-DPM}]/[\text{DPM}]=k_2/k_3\cdot k_{-1}/k_{-2} \quad (7)$$

The facility of the bond cleavage in the R-DPM (I), k_{-2}/k_{-1}, can be evaluated by Eq. (6) or (7). The value of k_2/k_3 is determined by the competitive benzylation between IV and V under the influence of the catalyst, which does not exhibit any ability to cleave the DPM.[8)]

The value of k_2/k_3, which was obtained by the competitive benzylation of benzene and chlorobenzene with benzyl chloride under the influence of aluminum chloride-nitromethane, was found to be 0.21;[2)] the average concentrations of DPM, Cl-DPM, and Cl_2-DPM at equilibrium in the cleavage reactions of DPM, Cl-, and Cl_2-DPM in the mixture of benzene and chlorobenzene were 37.8, 49.5, and 8.5 mol% respectively (Table 4 in Part IV[4)]).

When we introduce these values into Eq. (6) or (7), k_{-1}/k_{-2} is 1.47 or 1.07 respectively.

The concentration of the DPM at equilibrium in the cleavage reaction can be calculated on the basis of the above data. If $k_{-1}/k_{-2}=1.47$ is used, [Cl-DPM]/[DPM]$=0.21\times1.47+1=1.31$ and [Cl_2-DPM]/[DPM]$=0.21\times1.47=0.31$. If k_{-1}/k_{-2} is

TABLE 2. THE CALCULATED AND OBSERVED VALUES OF PRODUCT CONCENTRATIONS AT EQUILIBRIUM IN THE CLEAVAGE REACTION

	Product, mol%		
In the case of R=Cl,	DPM	Cl-DPM	Cl_2-DPM
$k_{-1}/k_{-2}=1.47$	38.1	50.0	11.9
$k_{-1}/k_{-2}=1.07$	40.9	50.0	9.1
Calculated (average)	39.5	50.0	10.9
Observed (average)	37.8	49.5	8.5
In the case of R=Me,	DPM	Me-DPM	Me_2-DPM
$k_{-1}/k_{-2}=0.05$	43.1	50.0	6.9
$k_{-1}/k_{-2}=0.08$	39.7	50.0	10.3
Calculated (average)	41.4	50.0	8.6
Observed (average)	41.3	47.8	11.1

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7) The apparent reactivity of *p*-chlorobenzyl chloride was equal to that of benzyl chloride under the influence of aluminum chloride - nitromethane.[2)]

8) G. A. Olah, S. J. Kuhn and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962).

TABLE 3. THE COMPETITIVE BENZYLATION OF BENZENE AND TOLUENE WITH BENZYL CHLORIDE[a)]

Run	Time min	Temp. °C	Catalyst	Product, mol%			S_f[e)]	k_T/k_B[f)]	Isomer of Me-DPM, %		
				DPM	Me-DPM	Me_2-DPM			ortho	meta	para
1[b)]	1	20	$AlCl_3$	16.4	80.6	3.0	0.943	4.91	39.1	11.3	49.6
2	1	20	$AlCl_3$	24.6	59.2	16.2	—	—	18.0	58.0	23.3
3	60	50	$AlCl_3$	42.3	46.2	11.5	—	—	11.1	64.7	24.2
4	30	50	$InCl_3$	9.8	90.2	—	1.377	9.20	40.9	4.6	54.5
5[c)]	30	25	$AlCl_3$-$MeNO_2$	23.8	76.2	—	1.367	3.20	43.5	4.5	52.0
6[d)]		25	$GaBr_3$				0.609	4.00	41.1	17.4	39.5

a) The molar ratio of benzene, toluene and the catalyst to the chloride was 10, 10 and 0.1 respectively.
b) The catalyst: 0.01 molar ratio.
c) Data were quoted from Ref. 8.
d) Data were quoted from Ref. 9.
e) Intramolecular selectively, $S_f = \log 2 \times \%\ \text{para}/\%\ \text{meta}$
f) Intermolecular selectivity: the ratio of rate constants of benzene and of toluene.

1.07, [Cl-DPM]/[DPM]=1.22 and [Cl_2-DPM]/[DPM]=0.22 are obtained.

On the other hand, if k_2/k_3 $(=k_T/k_B)=3.20$ (a value which was obtained by the competitive benzylation of benzene and toluene[8)] (Run 5 in Table 3)), and if the average concentrations at equilibrium given in Table 1 are introduced into Eq. (6) or (7), k_{-1}/k_{-2} is 0.05 or 0.08 respectively.

The concentration of the DPM at equilibrium in the cleavage reaction can be calculated in the way which has been described above. If k_{-1}/k_{-2} is 0.05, [Me-DPM]/[DPM] and [Me_2-DPM]/[DPM] are 1.16 and 0.16 respectively. If $k_{-1}/k_{-2}=0.08$ is applied, [Me-DPM]/[DPM] and [Me_2-DPM]/[DPM] are 1.26 and 0.26 respectively.

On the basis of the above data, the calculated and observed [DPM], [R-DPM] and [R_2-DPM] values at equilibrium in the cleavage of Cl-DPM or Me-DPM are summarized in Table 2.

Thus, the facility of the bond cleavage, k_{-1}/k_{-2}, is affected by the relative basicities of the two aromatic rings in the R-DPM; in other words, the bond in the side of the aromatic ring with a higher basicity is more cleft than the other. Also, the product distribution is affected by the basic strength of the benzene derivatives, IV and V, which are present in the reaction system as well as by the relative basicities of the two aromatic rings in the R-DPM.

The Competitive Benzylation of Benzene and Toluene with Benzyl Chloride. The competitive benzylation of benzene and toluene with benzyl chloride was carried out under various conditions. The results, together with the data reported by Olah *et al.*[8)] and by Brown and Bolto,[9)] are shown in Table 3.

The compositions of the equilibrium mixture (Run 3) are similar to those of the cleavage of DPM or Me-DPM given in Table 1. Olah and his co-workers[8)] established that the intermolecular and intramolecular selectivities, k_T/k_B and S_f, which were obtained by using the competitive benzylation of benzene and toluene under the influence of aluminum chloride-nitromethane, were 3.20 and 1.367 respectively (Run 5). On the other hand, by utilizing the competitive benzylation under the influence of gallium bromide, k_T/k_B and S_f were established to be 4.0 and 0.609 respectively (Run 6).[9)]

It has generally been accepted that, in the electrophilic substitution, the intermolecular and intramolecular selectivities are affected by the activity of reactive species, that is, by the cation entity.[10)]

It is supposed that the reactivity of the benzyl cation entity in the benzylation is greatly affected by the activity of catalyst. Although the cleavage reaction took place to a small extent even under the influence of a trace of aluminum chloride (Run 1), the calculated values of k_T/k_B and of S_f are approximately established to be 4.91 and 0.943 respectively. In particular, the value of S_f is fairly different from the reported values. Although Brown *et al.* did not mention the kinds of product, it may be considered that the cleavage reaction took place largely under these conditions.

Under the influence of indium chloride, which does not exhibit the ability to cleave the DPM (Run 4), the values of k_T/k_B and of S_f were established to be 9.20 and 1.377 respectively. While the value of S_f is almost equal to Olah's value, the value of k_T/k_B is considerably larger than the reported value.

Consequently, it may be considered that, in the benzylation which the cleavage reaction does not accompany, the intermolecular selectivity is affected by the activity of the catalyst, while the intramolecular selectivity is not.

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9) H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3220 (1959).

10) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

TABLE 4. THE BENZYLATION OF TOLUENE WITH BENZYL CHLORIDE UNDER THE INFLUENCE OF ALUMINUM CHLORIDE[a)]

Run	Time min	Temp. °C	Product, mol%			Isomer of Me-DPM			S_f
			DPM	Me-DPM	Me$_2$-DPM	ortho	meta	para	
1	1/6	20	0.8	86.9	12.3	36.4	13.7	49.9	0.862
2[b)]	1	20	—	91.0	9.0	36.8	10.1	53.1	1.022
3	1	20	2.2	44.0	53.8	14.1	63.9	22.0	—
4	5	50	0.5	14.0	85.5	16.6	55.0	28.4	—
5	10	50	0.5	13.7	85.8	12.0	57.2	30.8	—
6	60	50	0.5	15.0	84.5	11.9	58.2	29.9	—
7[c)]	30	50	—	100	—	42.9	3.2	53.9	1.528

a) The molar ratio of toluene, the chloride and the catalyst was 20, 1.0 and 0.1 respectively.
b) The catalyst: 0.008 molar ratio.
c) Aluminum chloride - nitromethane was used as catalyst.

TABLE 5. THE BENZYLATION OF TOLUENE WITH BENZYL CHLORIDE UNDER VARIOUS CATALYSTS AT 113°C*

Run	Catalyst	Time hr	Product, mol%			Isomer of Me-DPM, %			S_f
			DPM	Me-DPM	Me$_2$-DPM	ortho	meta	para	
1	Zn-Hg	5	—	59.7	—	46.3	0.4	53.3	2.426
2	FeCl$_3$	6	—	76.4	—	46.6	0.5	52.9	2.326
3	ZnCl$_2$	6	—	66.0	—	45.9	2.0	52.1	1.717
4	Cu	6.5	—	73.3	—	52.2	1.6	46.2	1.762
5	Al-Hg	2.5	1.6	18.2	55.9	18.2	59.0	22.8	—
6	CdCl$_2$	6.5	—	72.3	—	49.6	0.5	49.9	2.300
7	SnCl$_4$	6.5	—	79.9	—	46.8	1.7	51.5	1.782
8	CoCl$_2$	5	—	70.5	—	40.3	1.5	58.2	1.889
9	TiCl$_4$	4.5	—	72.4	—	43.0	4.3	52.7	1.389

* The molar ratio of toluene, the catalyst and the chloride was 10, 0.1 and 1.0 respectively.

The Benzylation of Toluene under the Influence of Aluminum Chloride. Since the kinds of products in the benzylation are affected by the cleavage reaction, as has been mentioned previously, an investigation of the isomer distributions will be meaningless unless the cleavage reaction is taken into consideration.

In order to obtain clearer information concerning the relation between the cleavage reaction and the isomer distribution of Me-DPM, aluminum chloride-catalyzed benzylations of toluene were carried out under various conditions. The results are summarized in Table 4.

In Runs 1 and 2, the formation of Me$_2$-DPM in about 10 mol% suggests that the cleavage reaction took place to a small extent even when the reaction time was quite short or in the presence of a trace of the catalyst. In these cases, however, *m*-Me-DPM was formed in a small amount and the isomer distribution of Me-DPM is similar to that in Run 7, in which the cleavage reaction does not take place. On the other hand, when the cleavage reaction was obvious (Runs 3—6), the isomer distributions are fairly different from the data in Run 7.

In other words, the smaller the extent of the cleavage reaction is, the closer the value of the intramolecular selectivity, S_f, approaches that in the case when the cleavage reaction does not take place.

The Benzylation of Toluene under Various Catalysts. In connection with the preparation of Me-DPM, the benzylation of the toluene was carried out under various catalysts in order that the relation between the properties of the catalysts and the isomer distribution of Me-DPM could be examined. In view of the method of preparation in these cases, large-scale reactions were carried out until the evolution of hydrogen chloride ceased. The fraction (bp 138—143°C/11 mmHg) was obtained by the distillation of the reaction mixtures; it was analyzed by gas chromatography and by the infrared spectroscopic method described above. The results are shown in Table 5.

As is shown in Table 5, the catalysts other than the aluminum amalgam exhibit no ability to cleave the DPM. In the presence of the aluminum amalgam, however, more *m*-isomer was formed than *m*-Cl-DPM in the benzylation of chlorobenzene under the influence of the same catalyst.[2)] On the other hand, the isomer distributions of Me-DPM in the presence of other catalysts were similar

Table 6. The competitive benzylation of benzene and toluene under the influence of indium chloride at 40°C

Toluene/Benzene[a]	Observed[a] Me-DPM/DPM	Calculated[a] Me-DPM/DPM
0.28	2.23	8.08
0.93	7.09	9.24
2.45	24.87	10.05

a) Molar ratio.

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

to that of Run 7 in Table 4.

In this connection, the values of S_f were calculated in all runs except Run 6. Although the values of S_f are not always accurate, in that *m*-isomer is formed in only a small amount, they are considerably larger than that reported by Brown *et al.*[9)]

In the same manner as in the preceding paper,[2)] the competitive indium chloride-catalyzed benzylation of benzene and toluene was carried out by changing the concentrations of the aromatics. The results are shown in Table 6.

As is shown in Table 6, the molar ratio (average 9.12) of Me-DPM to DPM remains almost unchanged if the first-order dependence on the aromatics is accepted. The relative reactivity of toluene against benzene, that is, the intermolecular selectivity (k_T/k_B), was about 9.12. The value is quite different from Olah's value (3.20), obtained by the competitive aluminum chloride - nitromethane catalyzed benzylation.[8)]

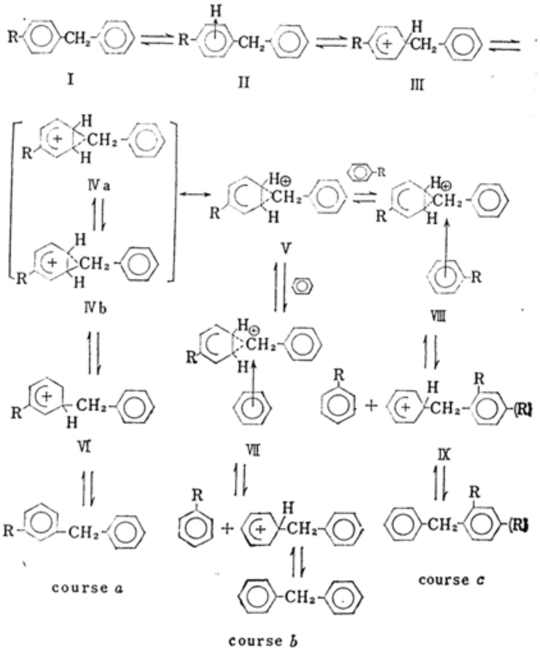

Chart 2.

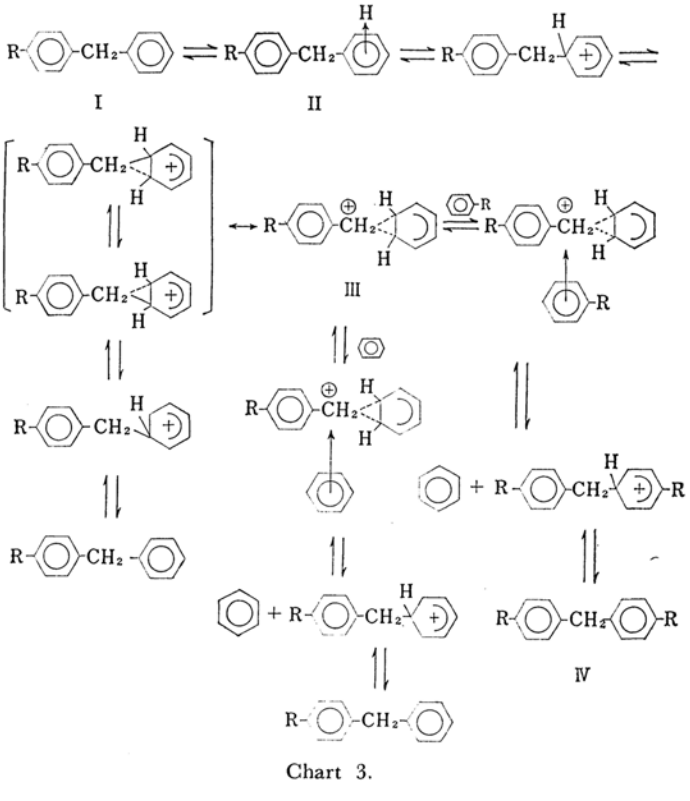

Chart 3.

This fact suggests that, in the presence of indium chloride, which exhibits a weaker catalytic activity, the benzyl cation entity reacts more easily with a higher basic toluene than with a lower basic benzene in comparison with the influence of aluminum chloride - nitromethane, which exhibits a stronger activity.

A Discussion of the Isomerization Mechanism. The cleavage reaction and isomerization take place in the benzylation under the influence of aluminum chloride or gallium chloride. Consequently, any discussion of the isomer distribution will be meaningless unless the cleavage reaction is taken into consideration.

As has been mentioned above, the intramolecular selectivity by which the isomer distribution is defined is not affected by the activity of the catalyst, but the formation of the *m*-isomer is due mainly to a secondary reaction.

It is known that alkylbenzene is intramolecularly isomerized by the 1, 2-shift mechanism.[11] In the benzylation under the influence of aluminum chloride or gallium chloride, however, the cleavage of the DPM is usually present also. Accordingly, the intramolecular and intermolecular isomerization should be considered concurrently.

On the basis of the above viewpoint, the mechanisms of the cleavage and of the isomerization of the DPM are suggested in Charts 2 and 3. Here, we shall discuss *p*-R-DPM (I).

Chart 2 shows that where the π-complex (II) between the substituted benzene ring in I and proton is formed, the isomerization by the cleavage takes place other than by the 1, 2-shift mechanism (Course a). If the oriented π-complex (V) formed through III and IV reacts with the benzene present in a large amount, DPM is formed by the cleavage (Course b). On the other hand, if V reacts with mono-substituted benzene, *o*- and/or *p*-R-DPM are formed through Course c (the isomerization by the cleavage).

Since the σ-complex (VI) of *m*-R-DPM formed by the 1, 2-shift mechanism is most stable among the isomers,[12] it can be said that *m*-R-DPM is formed in a large amount.

On the other hand, if the π-complex (II) between the benzene ring in *p*-R-DPM (I) and the proton is formed, the oriented π-complex (III) will react with benzene to give nonisomerized R-DPM, and with mono-substituted benzene to form di-substituted DPM (IV) (Chart 3).

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[11] G. A. Olah, M. W. Meryer and N. A. Overchuck, *J. Org. Chem.*, **29**, 2313 (1964).

[12] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).