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# Studies of Diarylalkanes. IV.*1, 1) The Cleavage of Diphenylmethanes under the Influence of Aluminum Chloride in the Binary Mixture of Benzene with Chlorobenzene

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The reactions of DPM and its chloro derivatives with aluminum chloride in a mixture of benzene and chlorobenzene have been studied in order to obtain clearer information concerning the bond cleavage of the diarylmethanes. The constants or the activation energy of the cleavage reaction have been determined, and it has found that, in such reactions, a first-order dependence on the aromatic substrate exists; an equilibrium relationship consisting of four systems has been an equilibrium relationship consisting of four systems has been established among the products. The isomer distribution of the Cl-DPM which was formed by the cleavage of DPM or 4-Cl-DPM exhibited a marked variation with the reaction time. These results show that the cleavage reaction is closely connected with Friedel-Crafts benzylation.

In previous papers1,2) dealing with the cleavage of diarylmethanes under the influence of aluminum chloride, it was established that the bond between the aromatic ring and the methylene group is cleft and that the cleavage is mainly affected by the relative basicities of the two aromatic rings in the diarylmethane as well as by the basic strength of the benzene derivative which is present in the reaction system.

In the present work, the cleavage reaction of diphenylmethane (DPM) and its chloro derivatives in a mixture of benzene and chlorobenzene was studied in order to obtain clearer information concerning the bond cleavage of chlorodiphenylmethane (Cl-DPM), for, in the case of the cleavage in the absence of a solvent, more chlorobenzene, which exhibits a lower basicity than benzene, was formed than benzene.1)

## Experimental

**Materials.** DPM and those of its derivatives used in this work were prepared by the reported method and were purified by fractional distillation and/or recrystallizations. The physical constants for these compounds are listed in Table 1.

Aluminum chloride (reagent grade of the Wako Pure Chemical Industries, Ltd.) was purified by sublimation just before the reaction.

**Solvent.** Benzene (bp 80°C) was distilled and dried over metallic sodium wire, and chlorobenzene (bp 132°C) was purified by distillation.

**General Kinetic Method.** After a solution of a definite amount of DPM in a mixture of 10 mol of benzene and 10 mol of chlorobenzene per mole of DPM in a reaction flask similar to one described previously2) had been maintained at a desired, constant

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[*1] Presentedi n part at the General Meeting of the Kyushu, Chugoku and Shikoku Districts of the Chemical Society of Japan, Kagoshima, December, 1963.

1) Part III: O. Tsuge and M. Tashiro, This Bulletin, **38**, 184 (1965).

2) O. Tsuge and M. Tashiro, *Coal Tar (Koru Taru)*, **14**, 513 (1962).

TABLE 1. THE PHYSICAL CONSTANTS OF DIPHENYLMETHANES

| Compound | Bp °C/mmHg | Mp °C | $n_D^{25}$ | R. T.[c] min |
|---|---|---|---|---|
| DPM[a] | 140—141/5 | 25 | — | 4.6 |
| 2-Chloro[b] | 127—128/1.5 | — | 1.5915 | 6.1 |
| 3-Chloro[b] | 163—166/12 | — | 1.5892 | 7.0 |
| 4-Chloro[b] | 130—135/3 | — | 1.5885 | 7.9 |
| 4,4′-Dichloro[b] | 147—154/3 | 56—57 | — | 14.8 |

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

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

c) Retention time (R. T.) under the following condition: column, 30% high vacuum silicon grease; column temperature, 235°C; carrier gas, hydrogen, 22 ml/min.

temperature in a thermostat, 0.1 mol of aluminum chloride per mole of DPM was added to the reaction mixture. One-milliliter aliquots of this solution were withdrawn from time to time by means of a pipet; these portions were quenched with ice-cold dilute hydrochloric acid. After the quenched products had been extracted with ether, the ether solution was washed well with water, dried over anhydrous sodium sulfate, and then analyzed by gas chromatography.

In the case of the reaction in which a small amount of water was used as a co-catalyst, the DPM was added to a mixture of benzene, chlorobenzene, aluminum chloride, and water.

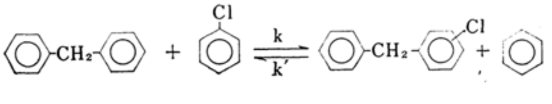
**Analytical Procedure.** The analyses were carried out by gas chromatography using a Shimadzu Gas Chromatograph, GC-IB. The conditions for gas chromatographic analyses were as follows: column, 30% high-vacuum silicon grease, 2 m; temperature, 235°C; carrier gas, hydrogen, 22 ml/min.

From the areas of individual peaks, mol% figures were calculated for each product after the relative response data had been determined by the internal standard method. Individual peaks were identified by the retention times of pure samples.

## Results and Discussion

**The Cleavage of DPM in the Mixture of Benzene and Chlorobenzene.** Figure 1 shows the plots of the mol% of the products against the time for the reactions of DPM with aluminum chloride in the mixture of benzene and chlorobenzene at various temperatures. The molar ratios of aluminum chloride, benzene, and chlorobenzene to DPM were 0.1, 10 and 10 respectively.

In the initial stage of the cleavage reaction, in which $Cl_2$-DPM was formed in only a trace amount, it may be considered that the following equilibrium between DPM and Cl-DPM is established:



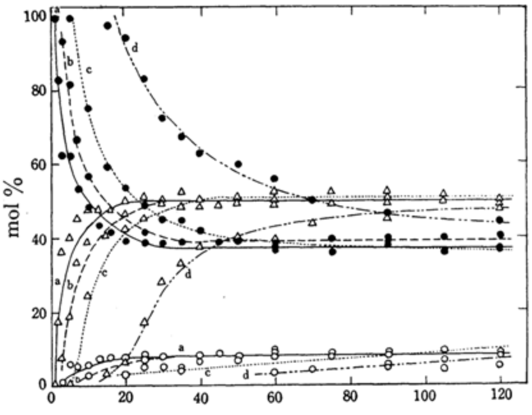


Fig. 1. Reactions of DPM with aluminum chloride in the mixture of benzene and chlorobenzene at various temperatures.
a) 70°C (——), b) 60°C (----), c) 50°C (······)
d) 40°C (—··—··)
● DPM, △ Cl-DPM, ○ $Cl_2$-DPM

The rate of the consumption of DPM in the initial stage may be approximately expressed as follows:

$$\frac{dx}{dt} = k(a-x) - k'x \qquad (1)$$

where $a$ is the initial concentration (mol%) of DPM, $x$ is the concentration of DPM consumed after $t$ sec, and $k$ and $k'$ are the rate constants of the consumption and the formation of DPM respectively. Moreover, the change in the concentrations of benzene and chlorobenzene may be negligible, since they were used as solvents.

If the concentration of Cl-DPM at the equilibrium is $x_e$,

$$k(a - x_e) - k'x_e = 0 \qquad (2)$$

From Eqs. (1) and (2), the rate of the consumption of DPM may be given by:

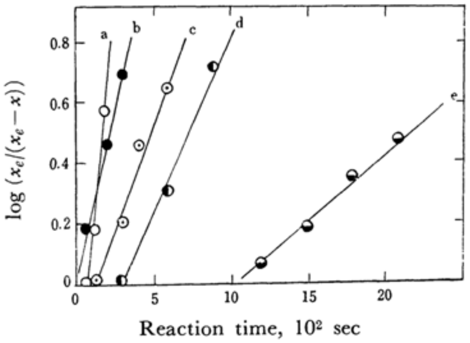


Fig. 2. Plots of the first order function against time.
a) 70°C, b) 50°C (water-promoted aluminum chloride), c) 60°C, d) 50°C, e) 40°C

$$\frac{dx}{dt} = ka(x_e - x)/x_e \qquad (3)$$

Equation (3) then gives:

$$k = \frac{2.303x_e}{at} \log \frac{x_e}{x_e - x}$$

The plots of $\log x_e/(x_e - x)$ *vs.* the reaction times show straight lines (Fig. 2); $x_e$ was a given a value of 50 mol%, since the $x_e$ value at each temperature was found to be about 50 mol%, as is shown in Fig. 1. In the reactions at lower temperatures, however, the straight lines did not pass through the zero point; this phenomenon may be ascribed to the presence of the induction period observed in Fig. 1. The rate constants, *k*, at 40, 50, 60, and 70°C were: $5.07 \times 10^{-4}$, $1.32 \times 10^{-3}$, $1.60 \times 10^{-3}$, and $4.75 \times 10^{-3}$ sec$^{-1}$ respectively.

Figure 3 shows the plots of the logarithm of the rate constants against the reciprocal absolute temperatures: the activation energy of the cleavage reaction was thus found to be 16.5 kcal/mole.

The use of water as a co-catalyst eliminates the necessity of maintaining reaction systems under rigidly anhydrous conditions. It was also observed that water as a co-catalyst had a strong effect on the isomerization and disproportionation of halobenzenes.[3)]

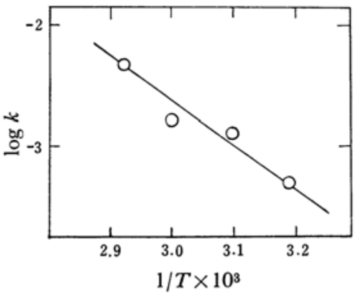


Fig. 3. Plots of the logarithm of the rate constants against the reciprocal absolute temperature.

A similar reaction using 0.1 mol of aluminum chloride and 0.025 mol of water per mole of DPM was carried out at 50°C. The first-order plots of the rate of the consumption of DPM in this case are also shown in Fig. 2; the rate constant was $2.88 \times 10^{-3}$ sec$^{-1}$, which was about 2.1 faster than that when aluminum chloride was used alone.

If the benzyl cation entities are formed in the cleavage reaction, as has been suggested in a preceding paper,[1)] it may be anticipated that the first-order dependence on the aromatic substrate may be established in such a cleavage reaction as well as observed in the Friedel-Crafts benzylation.[4,5)]

In order to establish whether a first-order dependence on the aromatic substrate in such cleavage reactions indeed exists, the reaction was carried out by changing the concentration of either benzene or chlorobenzene.

As may be seen in Table 2, the results show that the molar ratio of Cl-DPM to DPM remains almost unchanged even if the first-order dependence on the aromatic substrate concentration is accepted.

TABLE 2. THE FIRST-ORDER DEPENDENCE ON THE AROMATICS[a)]

| Chlorobenzene/[b)] Benzene | Observed[b)] Cl-DPM/DPM | Calculated[c)] Cl-DPM/DPM |
|---|---|---|
| 0.30 | 0.42 | 1.40 |
| 0.91 | 1.11 | 1.30 |
| 2.49 | 3.38 | 1.36 |
| | | Average 1.35 |

a) Mixtures of a definite amount of DPM, 20 mol of the combined aromatic substrate (benzene and chlorobenzene), and 0.1 mol of aluminum chloride per mole of DPM were heated at 70°C for 1 hr.

b) Molar ratio.

c) Molar ratio according to the first-order dependence on the aromatic substrate concentration.

**The Cleavage of 4-Cl-DPM in the Mixture of Benzene and Chlorobenzene.** A similar reaction of 4-Cl-DPM with water-promoted aluminum chloride was carried out at 50°C. The

TABLE 3. THE REACTION OF 4-Cl-DPM WITH WATER-PROMOTED ALUMINUM CHLORIDE IN THE MIXTURE OF BENZENE AND CHLOROBENZENE[a)]

| Time min | Product,[b)] mol % | | | Isomer distribution of Cl-DPM, % | | |
|---|---|---|---|---|---|---|
| | DPM | Cl-DPM | $Cl_2$-DPM | ortho | meta | para |
| 2 | 1.4 | 98.6 | — | — | — | — |
| 5 | 2.4 | 97.6 | — | — | — | — |
| 11 | 15.3 | 84.7 | — | 2.4 | — | 97.6 |
| 15 | 40.4 | 59.6 | — | 8.2 | — | 91.8 |
| 20 | 58.9 | 41.1 | — | 34.6 | — | 65.4 |
| 30 | 54.0 | 46.0 | — | 40.4 | 16.4 | 43.2 |
| 45 | 46.8 | 53.2 | — | 31.1 | 35.4 | 33.5 |
| 60 | 38.5 | 55.3 | 4.4 | 21.1 | 52.9 | 26.0 |
| 90 | 33.9 | 52.6 | 9.7 | 23.4 | 52.6 | 24.0 |
| 130 | 34.0 | 51.4 | 9.6 | 23.4 | 51.1 | 25.5 |

a) Mixture of 4-Cl-DPM (10.23 g), aluminum chloride (0.79 g) and water (22.5 $\mu l$) in benzene (39.22 g) and chlorobenzene (56.35 g) was heated at 50°C.

b) Anthracene (2—8 mol%) was formed.

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[3)] G. A. Olah, W. S. Tolgyesi and R. E. A. Dear, *J. Org. Chem.*, **27**, 3441 (1962).

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

[5)] G. A. Olah, S. J. Kuhn and S. H. Flood, *ibid.*, **84**, 1695 (1962).

TABLE 4. THE PRODUCTS AT EQUILIBRIUM IN THE CLEAVAGE OF DPM, 4-Cl- AND 4, 4′-$Cl_2$-DPM WITH ALUMINUM CHLORIDE IN THE MIXTURE OF BENZENE AND CHLOROBENZENE*

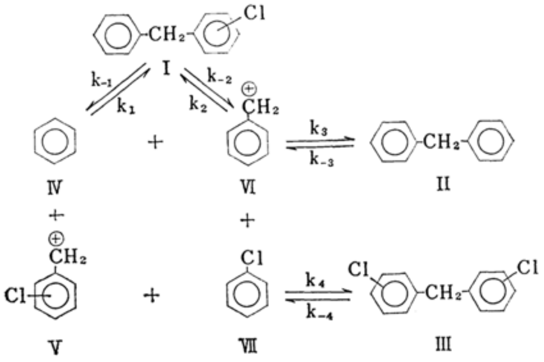
| Run | Compound | Temp. °C | Time min | Product, mol % | | | | Isomer of Cl-DPM, % | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | DPM | Cl-DPM | $Cl_2$-DPM | Anthracene | ortho | meta | para |
| 1 | DPM | 40 | 120 | 39.2 | 50.3 | 6.5 | 4.0 | 22.5 | 54.1 | 23.4 |
| 2 | DPM | 50 | 60 | 36.1 | 50.7 | 7.6 | 5.6 | 22.7 | 54.2 | 23.1 |
| 3 | DPM | 60 | 60 | 38.8 | 51.0 | 6.7 | 3.5 | 24.1 | 50.9 | 25.0 |
| 4 | DPM | 70 | 60 | 38.2 | 49.1 | 7.3 | 5.4 | 23.2 | 51.9 | 24.9 |
| 5 | 4-Cl-DPM | 70 | 60 | 37.2 | 48.3 | 9.4 | 5.1 | 21.1 | 52.9 | 26.0 |
| 6 | 4, 4′-$Cl_2$-DPM | 70 | 60 | 32.6 | 51.5 | 14.3 | 1.6 | 20.6 | 53.7 | 25.7 |
| | | | | (36.5) | (48.2) | (13.5) | | | | |
| | | | Calculated: | 41 | 50 | 9 | | | | |

* The DPM was reacted with aluminum chloride (0.1 mol) in the mixture of benzene (10 mol) and chlorobenzene (10 mol) per mole of the DPM respectively.

variations in products affected by the reaction times, together with the isomer distributions of Cl-DPM, are shown in Table 3.

**The Equilibrium Relationship.** The products and the isomer distributions of Cl-DPM in the cleavage reaction of DPM, 4-Cl- and 4, 4′-$Cl_2$-DPM with aluminum chloride in the mixture of benzene and chlorobenzene are summarized in Table 4. The parentheses in run 6 indicate the values corrected according to the first-order dependence on the aromatic substrate mentioned in Table 2, because the molar ratio of chlorobenzene to benzene changed from 1.00 before the reaction to 1.20 after it.

On the basis of the available data, it seems reasonable to conclude that the following equilibrium relationship, consisting of four systems, has been established in such cleavage reactions:



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 the consumption of the I, II and III diphenylmethanes respectively.

Consequently, the relative facility of the bond cleavage of I should be estimated by $k_{-2}/k_{-1}$, not by the molar ratio of the chlorobenzene (VII) formed to benzene (IV).

If it is assumed that the relative reactivities of the benzyl cation entities, V and VI, in the above scheme are equal to each other,⁶⁾ $k_1=k_3$ and $k_2=k_4$. On the other hand, the relative benzylation rate of chlorobenzene to benzene was measured by the competitive benzylation method described in a preceding paper¹⁾: $k_{\text{Cl-benzene}}/k_{\text{benzene}} = 0.21$, where $k_{\text{benzene}}$ and $k_{\text{Cl-benzene}}$ correspond to $k_3$ and $k_2$ in the above scheme respectively. That is, $k_2/k_3=0.21$.

On the basis of the above considerations, the molar ratios of the products, I, II and III, in the cleavage reactions in the presence of a large amount of benzene and chlorobenzene were calculated to be as follows: Cl-DPM (I), 1.21 (*ca.* 50 mol%);

TABLE 5. THE ISOMER DISTRIBUTION OF Cl-DPM IN THE CLEAVAGE REACTION OF DPM WITH WATER-PROMOTED ALUMINUM CHLORIDE*

| Time, min | Isomer of Cl-DPM, % | | |
|---|---|---|---|
| | ortho | meta | para |
| 1 | 35.4 | — | 64.6 |
| 3 | 44.3 | — | 55.7 |
| 5 | 48.5 | — | 51.5 |
| 10 | 43.0 | 13.8 | 43.2 |
| 16 | 35.6 | 31.7 | 32.7 |
| 20 | 32.4 | 36.4 | 31.2 |
| 30 | 27.5 | 45.6 | 26.9 |
| 40 | 26.7 | 49.7 | 23.6 |
| 50 | 25.5 | 47.0 | 27.5 |
| 60 | 23.9 | 52.2 | 23.9 |
| 80 | 23.7 | 50.9 | 25.4 |
| 120 | 23.2 | 52.9 | 23.9 |

* Mixture of DPM (12.71 g), aluminum chloride (1.03 g) and water (35 *μl*) in benzene (58.47 g) and chlorobenzene (84.40 g) was heated at 50°C.

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6) It will be reported in the next paper that, in the competitive benzylation of benzene and chlorobenzene under the influence of the aluminum chloride-nitromethane complex catalyst, benzyl and *p*-chlorobenzyl chloride exhibited almost the same reactivity.

DPM (II), 1.00 (*ca.* 41 mol%); $Cl_2$-DPM (III), 0.21 (*ca.* 9 mol%).

As is shown in Table 4, the calculated values show a good agreement with the observed values. It may be considered that the cleavage reaction is controlled by the relative basicities of benzene and chlorobenzene.

**The Isomer Distribution of Cl-DPM.** The isomer distributions of Cl-DPM in the cleavage reactions of DPM and 4-Cl-DPM with water-promoted aluminum chloride in the mixture of benzene and chlorobenzene were investigated at 50°C. The results are presented in Tables 3 and 5. Furthermore, the isomer distributions at equilibrium in the cleavage reactions of DPM, 4-Cl- and 4, 4'-$Cl_2$-DPM with aluminum chloride are shown in Table 4.

As is shown in Tables 3 and 5, the isomer distribution exhibited a marked variation with the reaction time. Furthermore, the Cl-DPM at equilibrium in the cleavage reactions of DPM, 4-Cl- and 4, 4'-$Cl_2$-DPM contains about 21—24% *o*-, 51—54% *m*-, and 22—26% *p*-isomer.

On the other hand, the diarylmethane was not cleft in the presence of such nitro compounds as nitroalkane or nitrobenzene, for these compounds formed complexes with aluminum chloride.

Olah and his co-workers⁴⁾ reported that the isomer distribution of Cl-DPM in the benzylation of chlorobenzene under non-isomerizing conditions was as follows: *o*-, 33.0%; *m*-, 0.6%; *p*-, 66.4%. These values are similar to those in the initial stage of the cleavage of DPM. It may be considered that the isomer distribution in the benzylation is related to the cleavage of the formed Cl-DPM. The relationship between the cleavage reaction and the benzylation will be discussed in the next paper.

The authors wish to thank Miss Akiko Kawano for her technical assistance.