Studies of Diarylalkanes. III.[*,1] The Cleavage of Diarylmethanes under the Influence of Aluminum Chloride

By Otohiko TSUGE and Masashi TASHIRO

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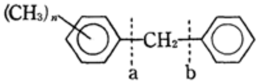
In the course of the study of the reaction of diarylalkanes with Friedel-Crafts catalysts, an investigation was carried out in order to find how various diarylmethanes cause cleavage under the catalytic influence of aluminum chloride.

It was reported in the preceding paper[1] that, under the influence of aluminum chloride, while diphenylmethane gives benzene, toluene, methyldiphenylmethane, dimethyldiphenylmethanes and anthracene, methyl-substituted diphenylmethanes give trimethylbenzene and dimethylanthracene beside the above products. It was also found that, in the case of methyldiphenylmethanes (I), the bond a is more easily cleft than the bond b and that the facility of the cleavage of the former is increased by increasing the number of methyl groups at the benzene ring, if the facility of the bond cleavage is estimated by the molar ratio of methylbenzene to the benzene which is formed by the cleavage. In other words, the higher the relative basicity of the methyl-substituted benzene ring in I, the more easily the bond a is cleft.



$n=1,2,3$

(I)

In the present work, the reaction of various diarylmethanes with aluminum chloride was studied in the absence of a solvent or by using excess aromatics as a solvent so that clearer information concerning the effect of the substituent could be obtained on the bond cleavage.

Results and Discussion

Diphenylmethane (II), 4-methyl- (III), 4-ethyl- (IV), 4-isopropyl- (V), 4-hydroxy- (VI), 2-hydroxy- (VII), 4-methoxy- (VIII), 2-methoxy- (IX), 4-chloro- (X), 4-phenyldiphenylmethane (XI) and 1-benzylnaphthalene (XII) were treated with aluminum chloride under various

TABLE I. REACTION OF EQUIMOLAR AMOUNTS OF 4-ETHYL- (IV), 4-ISOPROPYL- (V) OR 4-CHLORODIPHENYLMETHANE (X) AND ALUMINUM CHLORIDE AT 27°C FOR 2 hr.[a]

Run	Diphenylmethane	Product[b]												
		Benzene	Toluene	ArH[c]	ArH/Benzene	DPM[d]	C_1-DPM[d]	C_2-DPM[d]	C_3-DPM[d]	Cl-DPM[d]	Cl_2-DPM[d]	Anthracene	Unidentified	Residue[e]
1	IV	25.02	2.75	25.82	1.03	5.78	0.90	1.79	—	—	—	—	13.97 (14)[f]	47.19
2	V	22.65	4.02	19.46	0.86	5.33	0.84	5.41	3.70	—	—	—	14.60 (13)[f]	39.35
3	X	16.54	1.55	40.72	2.46	4.16	0.43	—	—	14.78	3.30	1.45	1.09 (2)[f]	36.99

a) Method A was applied to the analyses.
b) The amount of each product in this table and others is generally given as the mol.% to the starting material.
c) ArH: Ethyl-, isopropyl- and chlorobenzene are represented in the respective run.
d) DPM, C_1-DPM, C_2-DPM, C_3-DPM, Cl-DPM and Cl_2-DPM are represented diphenylmethane, methyl-, dimethyl-, trimethyl-, chloro- and dichlorodiphenylmethane respectively.
e) Weight % to the starting material.
f) Parentheses relate to a number of component.

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[*] Presented in part at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[1] Part II: O. Tsuge and M. Tashiro, *The Coal Tar (Koru Taru)*, **14**, 513 (1962).

TABLE II. REACTION OF VARIOUS DIARYLMETHANES WITH ALUMINUM CHLORIDE[a] AND RELATIVE REACTIVITIES OF AROMATIC COMPOUNDS

Run	Diarylmethane	Benzene	ArH		ArH/Benzene	Relative reactivity (ArH/Benzene)	Residue[b]
4	IV	33.3	37.1	Ethylbenzene	1.11	2.42[f]	35.9
5	V	34.7	29.3	Isopropylbenzene	0.84	2.22[f]	43.5
6	VI	17.5	25.7	Phenol	1.46	8.15[g]	37.5
7[c]	VI	30.4	71.5	Phenol	2.35	—	25.5
8	VII	25.8	39.8	Phenol	1.54	—	41.5
9[c]	VII	29.1	70.9	Phenol	2.43	—	25.4
10	VIII	26.6	39.1[d]	Anisole	1.45	6.77[g]	45.3
11	IX	22.7	38.4[e]	Anisole	1.69	—	33.8
12	X	15.7	51.2	Chlorobenzene	3.25	0.21[g], 0.24[f]	35.4
13	XI	28.9	23.8	Biphenyl	0.82	3.85[g]	41.8
14	XII	36.0	19.6	Naphthalene	0.55	16.95[g]	59.7

a) Equimolar amounts of the diarylmethane and aluminum chloride were reacted at 100°C for 1 hr. and method A was used to the analyses.
b) Weight % to the starting material.
c) Three moles of aluminum chloride were used to hydroxydiphenylmethane.
d) Total mol.% of anisole (13.1), phenol (21.4) and cresols (4.6).
e) Total mol.% of anisole (14.3), phenol (17.4) and cresols (6.7).
f) Competitive benzylation by benzyl chloride and aluminum chloride - nitromethane complex (G. A. Olah, S. J. Kuhn and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962)).
g) Competitive benzylation by benzyl chloride and aluminum chloride - nitrobenzene complex (Present work).

conditions and the products were analyzed by a quantitative gas-liquid chromatographic method.

The Reaction in the Absence of a Solvent.—The reaction of IV, V and X with aluminum chloride was carried out under conditions similar to those described previously.[1] The results are shown in Table I.

As Table I shows, various unidentified products were obtained from IV or V; hence, it is difficult to give the relative facility of the bond cleavage. The data for nine diarylmethanes (IV—XII) which may imply the approximate relative facility are shown in Table II.

The relative reactivities of the aromatic compounds which showed good agreement with the known order of the relative stabilities of aromatic π-complexes, toluene$>$ethylbenzene$>$propylbenzene,[2] are also listed in Table II. The relative facility of the bond cleavage in I and IV is in accordance with the relative basicities of the two aromatic rings.

In the case of V, however, the bond in the side of benzene exhibited a higher reactivity for the cleavage than the other; this is inconsistent with the relative basicities of benzene and propylbenzene. This discrepancy may be attributed chiefly to the secondary formation of benzene by the dispropotionation of the products, in addition to the formation of unidentified substances.

In the cases of VI, VII, VIII and IX (runs 6—11), the corresponding aromatic compound (phenol or anisole) was formed more than benzene in the corresponding case. The amount of the aromatic compound in the cases of VIII and IX, however, is given as the total mol. % of anisole, phenol and cresols, since the reaction of anisole with aluminum chloride under the same conditions was found to afford anisole, phenol and cresols in 28.0, 56.8 and 15.2 mol. % yields respectively.

As is shown in runs 7 and 9, the more severely the reaction condition was used, the larger the amount of lower boiling compounds formed and the smaller the amount of resinous material. This suggests that the resinous material consisting of a mixture of polybenzyls is partially decomposed to regenerate the corresponding aromatics. This seems to conform with the fact that diphenylmethane is regenerated by heating the mixture of polybenzyl and benzene with a large amount of aluminum chloride.[3]

In spite of the lower basicity of chlorobenzene than benzene, more chlorobenzene than benzene was obtained in the cleavage X, as is shown in runs 3 and 12. Moreover, the amount of unidentified substances was smaller than that in the cases of the alkyl derivatives mentioned above. This seems to be due to the stability of the chlorobenzene formed by the cleavage. When an equimolar

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

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

TABLE III. REACTION OF EQUIMOLAR AMOUNTS OF SEVERAL DIARYLMETHANES AND ALUMINUM CHLORIDE IN THE PRESENCE OF SOLVENT (10 mol.) AT 70°C FOR 1 hr.[a)]

Run	Diarylmethane	Solvent	Product								
			Benzene	Cl-C_6H_5[b)]	Naphthalene	DPM[b)]	Cl-DPM[b)]	1-Bz-N[b)]	Cl_2-DPM[b)]	Anthracene	Residue[c)]
15	II	Chlorobenzene	126.3	836.9	—	1.2	21.8	—	15.5	28.8	16.7
16	X	Benzene	923.9	53.7	—	66.8	7.4	—	1.7	0.5	8.0
17	XII	Benzene	970.5	—	56.4	60.6	—	9.7	—	+[d)]	18.0

a) Method B was used to the analyses.
b) Cl-C_6H_5: Chlorobenzene, DPM: Diphenylmethane, Cl-DPM: Chlorodiphenylmethane, 1-Bz-N: 1-Benzylnaphthalene, Cl_2-DPM: Dichlorodiphenylmethane.
c) Weight % to the starting diarylmethane.
d) A plus-sign, +, means a trace amount.

amount of chlorobenzene and aluminum chloride was heated at 100°C for 1 hr. only unchanged chlorobenzene was recovered; this finding is also endorsed by Olah and his coworkers,[4)] who reported that chlorobenzene was not disproportionated by water-promoted aluminum chloride.

In the cases of XI and XII (runs 13 and 14), less biphenyl and naphthalene, respectively which exhibit a higher basicity than benzene, were formed than benzene.

On the basis of the data mentioned above, it may be considered that the diarylmethanes are divided into two groups which exhibit different tendencies of the bond cleavage.

The Reaction in the Presence of Excess Aromatic.—As it may be considered that the resinous material is composed of polybenzyls, it is anticipated that the reaction in the excess benzene derivative will cause a decrease in its formation.

The data for some diarylmethanes which have been treated in excess benzene or chlorobenzene are shown in Table III. As expected, the amount of resinous material decreased definitely in comparison with the data in Table II.

In the reaction of II in excess chlorobenzene (run 15), the II was almost all consumed, and chloro-, dichlorodiphenylmethanes[5)] and anthracene were obtained. It was also observed that the amount of benzene increased and that of chlorobenzene decreased. In the similar reactions of X and XII in excess benzene (runs 16 and 17), similar phenomena were observed, where X and XII were consumed and diphenylmethane was formed in yields of 66.8 and 60.8 mol.% respectively.

On the basis of these data, it may be considered that benzyl cation entities were formed as the intermediates in the cleavage process.[6)] In run 15, furthermore, more anthracene was formed than in run 16 or 17. This fact may be interpreted as follows. The self-condensation of the benzyl cation to dihydroanthracene, which easily converts to anthracene,[7)] can take place to some extent in chlorobenzene, since the attack of the benzyl cation on chlorobenzene is relatively slow as a result of the low basicity of chlorobenzene.

On the other hand, the attack of the benzyl cation on benzene is more predominant than the self-condensation in runs 16 and 17, because the basicity of benzene is higher than that of chlorobenzene.

From the data in runs 15 and 16, also, it seems reasonable to say that a reaction of this kind is reversible.

When 0.1 mol. of aluminum chloride and 20 mol. of benzene derivative were used with the diphenylmethanes, it was also observed that the bond cleavage took place and that only a small percentage of the resinous material was formed.[8)] The results in the reactions of III, X, XI and XII in 20 mol. of benzene are shown in Fig. 1.

As is shown in Fig. 1, an incubation which had been reported in the Friedel-Crafts alkylation of aromatics at a low temperature[9,10)] was observed, and toluene, chlorobenzene, biphenyl and naphthalene were formed in a ratio of about 5 mol. % to the benzene, respectively. It was also observed that diphenylmethane was invariably formed in a ratio of about 5 mol. % to the benzene in all cases.

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

[5)] Dichlorodiphenylmethanes are considered to be a mixture of bis(chlorophenyl)methanes.

[6)] H. C. Brown and M. Grayson (*J. Am. Chem. Soc.*, **75**, 6285 (1953)) reported that a benzyl cation entity in the Friedel-Crafts benzylation is not an ionized form, such as $C_6H_5\overset{\oplus}{CH_2}$, but a polarized form, $C_6H_5\overset{\oplus}{CH_2}\cdots\overset{\ominus}{AlCl_4}$.

[7)] R. Scholl and C. Seer, *Ber.*, **54**, 330 (1922).

[8)] In order to obtain the reproducibiliy of data, a 0.025 molar ratio of water was added to aluminum chloride.

[9)] T. M. Berry and E. E. Reid, *J. Am. Chem. Soc.*, **49**, 3142 (1927).

[10)] E. M. Marks, J. M. Almand and E. E. Reid, *J. Org. Chem.*, **9**, 13 (1944).

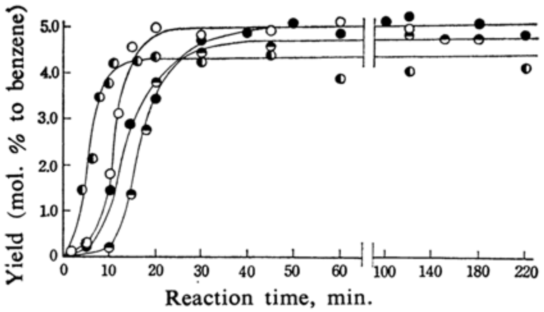

Fig. 1. Formation of the corresponding aromatic compounds by reactions of III, X, XI or XII (1.0 mol. respectively) with aluminum chloride (0.1 mol.) in the presence of benzene (20 mol.) at 50°C.

○ Toluene
● Chlorobenzene
◓ Biphenyl
◐ Naphthalene

On the basis of the apparent formation rates of the corresponding aromatics at the initial stage, the formation rate of chlorobenzene was considerably slower than those of naphthalene, toluene and biphenyl. This order is roughly in agreement with that of the relative basicity of the corresponding aromatic compounds.

In order to evaluate concurrently the effect of the two aromatic rings on the cleavage of the diarylmethane, the reactions of X in excess toluene and of III in excess chlorobenzene were carried out. The results are shown in Fig. 2.

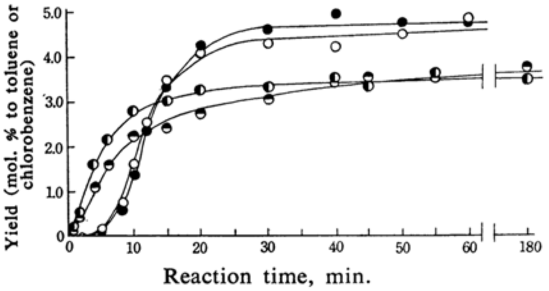

Fig. 2. Reactions of X (1.0 mol.) in toluene (20 mol.) and of III (1.0 mol.) in chlorobenzene (20 mol.) with aluminum chloride (0.1 mol.) at 50°C.

○ Benzene
● Chlorobenzene } in the reaction of X
◓ Benzene
◐ Toluene } in the reaction of III

Contrary to expectation, benzene and chlorobenzene were formed at nearly equal rates, as is shown in Fig. 2. However, the formation rate of toluene at the initial stage was faster than that of benzene. It may be considered that the contrast is due to the different strengths of the basicities of the chlorobenzene and toluene used as solvents.

Consequently, it is considered that the bond cleavage is affected by the basic strength of the benzene derivative which is present in the reaction system as well as by the relative basicities of the two aromatic rings in the diarylmethane.

Further investigation of the point in dispute is in progress; details will be published in the near future.

Resinous Material.—As has been mentioned above, the resinous material is composed of a mixture of polybenzyls. The resinous material in several runs was divided into three main fractions: the benzene-insoluble fraction (F_1), the benzene-soluble and petroleum ether-insoluble fraction (F_2) and the petroleum ether-soluble fraction (F_3). In general, F_1 was a higher melting black solid (m. p. above 200°C), F_2 was an orange-to-reddish brown powder (m. p. 60—100°C) and F_3 was an oily brown substance. As no suitable solvent of F_1 could be found, its molecular weight was not determined. The degree of the polymerization of F_2 and F_3 was about 5 to 8, like the polybenzyls, as judged by measuring their molecular weights by the Rast method.

Experimental

Materials.—The diarylmethanes were prepared by the reported method and were purified by fractional distillation and/or recrystallization. Diphenylmethane:[3] b. p. 140—141°C/5 mmHg, m. p. 25°C, retention time (hereafter referred to as R.T.[11]), 4.6 min.

4-Ethyldiphenylmethane:[12] b. p. 121 — 123°C/2 mmHg, n_{D}^{20} 1.5707, R.T., 7.0 min. 4-Isopropyldiphenylmethane:[13] b. p. 143—145°C/3 mmHg, n_{D}^{20} 1.5650, R.T., 9.5 min., 2-Hydroxydiphenylmethane:[14] b. p. 156—159°C/6 mmHg, m. p. 53—54°C, R.T., 8.5 min. 4-Hydroxydiphenylmethane:[15] b. p. 141—143°C/4 mmHg, m. p. 84°C, R. T., 10.5 min. 2-Methoxydiphenylmethane:[14] b. p. 148—152°C/9 mmHg, m. p. 31°C, R.T., 7.6 min. 4-Methoxydiphenylmethane:[15] b. p. 155°C/4 mmHg, n_{D}^{20} 1.5775, R.T., 9.1 min. 4-Chlorodiphenylmethane:[16] b. p. 130—135°C/3 mmHg, n_{D}^{20} 1.5885, R.T., 7.9 min. 4-Phenyldiphenylmethane:[17] b. p. 180—188°C/2 mmHg, m. p. 83—84°C, R.T., 43.1 min. 1-Benzylnaphthalene:[17] b. p. 175—179°C/5 mmHg, m. p. 57—58°C, R.T., 22.0 min.

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11) Column: 30% High vacuum silicon grease; Column temperature: 235°C; Carrier gas: H_2, 22 ml./min.

12) C. Söllscher, *Ber.*, **15**, 1680 (1882).

13) K. Allendorff, ibid., **31**, 1000 (1899).

14) L. Claisen, *Ann.*, **442**, 210 (1925).

15) W. F. Short and M. L. Steward, *J. Chem. Soc.*, **1929**, 555.

16) J. Blackwell and W. J. Hickinbotton, ibid., **1961**, 1405.

17) C. D. Nenitzescu, D. A. Isăcescu and C. N. Ionescu, *Ann.*, **491**, 210 (1931).

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

Procedure.—The experiments were carried out in an apparatus similar to one described previously.[1] Aluminum chloride was stirred into the diarylmethane at a constant temperature. After the specified reaction time, the reaction was quenched with dilute hydrochloric acid under ice-cooling.

The quenched product was treated by the following methods according to the individual case.

Method A.—When the product was contaminated with a fairly large amount of a resinous material (runs 1 to 14), this method was used. After the quenched product was subjected to steam distillation, the distillate f_1 was extracted with ether. The ether solution was washed well with water, dried over sodium sulfate, and analyzed by gas chromatography. The ether-insoluble residue was separated by a distillation into three fractions, the fraction f_2 distilling below 150°C (bath temperature), the higher boiling fraction f_3 distilling below 240°C (bath temperature)/1—2 mmHg, and the residual fraction. The fractions f_2 and f_3 were analyzed by gas chromatography.

Method. B.—When the amount of a resinous material was relatively small (runs 15 to 17), this method was applied. After being quenched, the reaction mixture was extracted with ether. The ether solution was washed with water to remove traces of acid and dried over sodium sulfate. The solution was divided by a distillation into three fractions, the lower boiling fraction f_1, the higher boiling fraction f_2, and residual fraction, as above. The distillates f_1 and f_2 were analyzed by gas chromatography.

Method C.—This method was used in the case of a reaction mixture in which a little resinous material was contained (Figs. 1 to 2). After the quenched product had been extracted with ether, the ether solution was washed well with water, dried over sodium sulfate, and immediately analyzed by gas chromatography.

Analytical Procedure.—The analyses were carried out by gas-liquid chromatography. The conditions for the gas chromatographic analyses were as follows. For the lower boiling fraction: column, 30% high vacuum silicon grease (HVSG) 2 m., temperature, 150°C, carrier gas, hydrogen, 30 ml./min. For the higher boiling fraction: column, 30% HVSG, 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 determining the relative response data by the internal standard method. Individual peaks were identified by means of the retention times of pure samples.

The Measurement of Relative Basicity.—The relative basicities of phenol, anisole, chlorobenzene, biphenyl and naphthalene to benzene were measured by a modification of Olah's method.[2]

Aluminum chloride (0.5 g.) dissolved in 20 ml. of nitrobenzene was vigorously stirred drop by drop into a mixture of benzyl chloride (8.7 mmol.), benzene (113 mmol.) and the corresponding aromatic compound (110 mmol.). After the addition of the aluminum chloride solution, the mixture was stirred at 30°C for another 30 min., and then it was quenched by the usual method. The quenched product was extracted with benzene, and the organic layer was washed well with water, dried over sodium sulfate, and analyzed by gas chromatography. The relative basicities of the corresponding aromatics were calculated by means of the molar ratio of the diarylmethane to diphenylmethane in each individual case.

Summary

The reaction of several diarylmethanes (III—XII) with aluminum chloride under various conditions has been carried out in order to elucidate the effect of the substituent on the cleavage of diarylmethanes. It has been established that the bond between the aromatic ring and the methylene group is cleft and that the cleavage is 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.

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The Research Institute of
Science and Industry
Kyushu University
Hakozaki, Fukuoka