Aromatic Arylation with Aryl Radicals. III. Gomberg Reaction in Dimethyl Sulfoxide

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Benzenediazonium tetrafluoroborate in dimethyl sulfoxide decomposed instantaneously with evolution of nitrogen upon addition of a dimethyl sulfoxide solution of choline or tetramethylammonium hydroxide. Orientations and partial rate factors for the phenylation of substituted benzenes indicated that the phenylating agent is not phenyl cation but phenyl radical. Hammett's plots of partial rate factors for *meta* and *para* substitutions were good straight lines with $\rho_m=0.34$, $\rho_p=1.63$ (in choline) and $\rho_m=0.48$, $\rho_p=1.69$ (in tetramethylammonium hydroxide solutions). Decomposition of benzenediazonium tetrafluoroborate by tetramethylammonium hydroxide in aqueous solution was also studied, and the orientation and partial rate factors for the phenylation of substituted benzenes were determined.

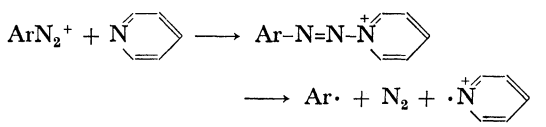
Arenediazonium salts decompose with evolution of nitrogen in aprotic polar solvents, and phenyl cation is considered to be the intermediate on the basis of the kinetic studies[1] and the partial rate factors for the competitive arylation of benzene and substituted benzenes.[2]

$$ArN_2^+ \longrightarrow Ar^+ + N_2 \qquad (1)$$

However, it has been reproted that arenediazonium salts undergo homolytic decomposition in methanol[3] or pyridine.[4]

$$\begin{aligned} ArN_2^+ + CH_3O^- &\longrightarrow Ar\text{-}N{=}N\text{-}OCH_3 \\ &\longrightarrow Ar\cdot + N_2 + \cdot OCH_3 \qquad (2) \end{aligned}$$

or



(3)

When an arenediazonium solution was added to a dimethyl sulfoxide solution of sodium nitrite, the diazonium salt decomposed instantaneously with evolution of nitrogen, and a homolytic decomposition mechanism was proposed.[5]

$$\begin{aligned} ArN_2^+ + NO_2^- &\longrightarrow Ar\text{-}N{=}N\text{-}O\text{-}N{=}O \\ &\longrightarrow Ar\cdot + N_2 + NO_2 \qquad (4) \end{aligned}$$

or

$$\begin{aligned} &2Ar\text{-}N{=}N\text{-}O\text{-}N{=}O \longrightarrow \\ &\quad Ar\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ar + N_2O_3 \\ &\quad \longrightarrow Ar\cdot + N_2 + Ar\text{-}N{=}N\text{-}O\cdot \qquad (5) \end{aligned}$$

As a continuation of our investigations on the decomposition of arenediazonium salts in aprotic polar solvents, addition of quaternary ammonium hydroxide to diazonium salts has been studied. It has been found that a reaction similar to the Gomberg reaction has taken place. With quaternary ammonium hydroxides the medium is homogeneous, whereas the ordinary Gomberg reactions are carried out in heterogeneous mixtures of water and aromatics.

In this paper, the results of this investigation will be described, and the evidence for the homolytic decomposition will be presented.

Experimental

Materials. Dimethyl sulfoxide was purified according to the method described in a previous paper.[1b)] Benzene, ethylbenzene, and chlorobenzene were washed with concentrated sulfuric acid and water successively, dried over calcium chloride, and distilled. Boiling points were 80, 135.7, and 131°C, respectively. Anisole was washed with an aqueous sodium hydroxide solution and water, dried over calcium chloride, and distilled; bp 153°C. Benzonitrile was purified by steam distillation. The distillate was washed with sodium carbonate solution and water, dried over calcium chloride, and distilled under reduced pressure; bp 123.4°C/100 mmHg. Nitrobenzene was washed repeatedly with a potassium dichromate solution, dried over calcium chloride, and distilled; bp 95.5°C/18 mmHg. Choline of Tokyo Kasei Limited was used without further purification. A 20% methanolic solution of tetramethylammonium hydroxide obtained from Aldrich Chemical Co., Inc. was evaporated under reduced pressure, and the residue was used.

Benzenediazonium tetrafluoroborate was prepared according to the directions described previously.[6]

Isomeric ethylbiphenyls, methoxybiphenyls, chlorobiphenyls, cyanobiphenyls, and nitrobiphenyls were prepared as the reference compounds by the methods described in the literature.[7] They were purified by elution chromatography, distillation or recrystallization, and their melting points and boiling points agreed with the values in the literature.

Phenylation of Monosubstituted Benzenes in DMSO. Under a nitrogen atmosphere a solution of 2.00 g of benzenediazonium tetrafluoroborate in 20 g of DMSO was added

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[1] a) E. S. Lewis, *J. Amer. Chem. Soc.*, **80**, 1371 (1958); b) K. Ishida, N. Kobori, M. Kobayashi, and H. Minato, This Bulletin, **43**, 285 (1970).

[2] a) R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc., B*, **1968**, 497; b) M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, This Bulletin, **43**, 215 (1970).

[3] D. F. DeTar and M. N. Turetzky, *J. Amer. Chem. Soc.*, **77**, 1745 (1955); **78**, 3925 (1956).

[4] R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).

[5] M. Kobayashi, H. Minato, N. Kobori, and E. Yamada, This Bulletin, **43**, 1131 (1970).

[6] E. B. Starkey, "Organic Syntheses," Coll. Vol. 2, p. 225 (1943).

[7] R. Adams, "Organic Reactions," Vol. II., John Wiley & Sons, Inc., London (1957); P. E. Fanta, *Chem. Rev.*, **64**, 613 (1954).

drop by drop at 20°C into a vigorously stirred solution of choline or tetramethylammonium hydroxide (3 mol/mol of PhN_2BF_4) and equimolar mixture of benzene and a substituted benzene (total aromatics, 50 mol/mol of PhN_2BF_4) in 60 g of DMSO. Evolution of nitrogen was instantaneous upon addition of each drop of the diazonium salt solution, and the addition was completed in about ten minutes. Ether was added to the solution, and the mixture was washed with water in order to remove DMSO and excess quaternary ammonium hydroxide. After it was dried over anhydrous magnesium sulfate, ether and about 70% of the aromatic solvents were evaporated, and biphenyl isomers in the residue were analyzed by gas chromatography with a Hitachi Gas Chromatograph K-53. Biphenyl isomers were identified by comparison of the retention times with those of the authentic samples on a 1 m to 6 m column (depending upon the ease of separation) packed with Chromosorb W (10% Apiezon L). Quantitative determinations were made by use of calibration curves.

Not benzene but chlorobenzene was used as the standard for the competitive phenylation, since unsubstituted biphenyl easily sublimes during the evaporation of substituted benzenes. The reactivity of each position of substituted benzenes was calculated relative to the reactivity of the *ortho* position of chlorobenzene. The partial rate factor of the *ortho* position of chlorobenzene was determined by a competitive phenylation of benzene and chlorobenzene without evaporation of the unchanged aromatics. The partial rate factors of various substituted benzenes were calculated by the following equation.

$$k_x/k = (k_x/k_{o\text{-Cl}}) \times (k_{o\text{-Cl}}/k)$$

where,

k_x/k: partial rate factor for phenylation of PhX at the *x* (*o*-, *m*-, or *p*-) position

$k_x/k_{o\text{-Cl}}$: relative rate of phenylation at the *x* position of PhX against that of the *ortho* position of chlorobenzene

$k_{o\text{-Cl}}/k$: partial rate factor for phenylation at the *ortho* position of chlorobenzene

Phenylation of Monosubstituted Benzenes in Water. Under a nitrogen atmosphere a solution of 2.20 g of benzenediazonium tetrafluoroborate in 35 g of water was added drop by drop at 20°C into a vigorously stirred solution of tetramethylammonium hydroxide (3 mol/mol of PhN_2BF_4) and equimolar mixture of benzene and a substituted benzene (total aromatics, 50 mol/mol of PhN_2BF_4) in 35 g of water. The reaction mixture was treated in a manner similar to that described above for the experiments in DMSO, and the product isomers were analyzed.

Results and Discussion

Benzenediazonium tetrafluoroborate in dimethyl sulfoxide (DMSO) decomposed instantaneously with evolution of nitrogen upon addition of a DMSO solution of choline ($HOCH_2CH_2(CH_3)_3N^+OH^-$) or tetramethylammonium hydroxide. Although the diazonium salts slowly decomposes even in the absence of these quaternary ammonium hydroxide, the rates of the first order decomposition yielding phenyl cation[2b] is much smaller than those observed in the presence of quaternary ammonium hydroxides. Therefore the mechanism of this rapid decomposition must be different from that involving phenyl cation. The difference of the mechanisms is also suggested by the absence of 1,3-benzoxathian in the products, which was always produced when phenyl cation was generated in DMSO.[2b]

TABLE 1. ORIENTATION (%) AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH PhN_2BF_4 IN DMSO AT 20°C

X in PhX	Additive	Orientation(%)			Partial Rate Factors		
		o-	*m*-	*p*-,	k_o/k	k_m/k	k_p/k
-OMe	A	62.7	24.2	13.1	3.21	1.23	1.33
	B	71.3	15.7	13.1	6.12	1.38	2.30
-Et	A	45.4	35.7	18.9	1.64	1.28	1.36
-Cl	A	55.9	24.2	19.9	3.69	1.60	2.63
	B	58.8	26.7	14.5	3.85	1.10	1.27
-CN	A	57.5	9.9	32.6	8.61	1.47	9.76
	B	67.2	11.3	21.5	18.8	3.51	12.0
$-NO_2$	A	59.8	6.7	33.5	16.6	1.87	18.7
	B	65.5	6.8	27.7	18.3	1.91	15.7

A: Choline=$HOCH_2CH_2(CH_3)_3N^+OH^-$
B: $(CH_3)_4N^+OH^-$

Table 1 shows the orientations and partial rate factors for the phenylation of substituted benzenes with benzenediazonium tetrafluoroborate and choline or tetramethylammonium hydroxide in DMSO. All the substituents behaved as *o,p*-directors, and the partial rate factors were always larger than 1. These data are similar to those of phenylation with phenyl radical produced from benzoyl peroxide[8] or *N*-nitrosoacetanilide[9] and quite different from those of phenylation with phenyl cation.[2,10] These findings indicate that the benzenediazonium salt reacts with quaternary ammonium hydroxide to produce phenyl radical.

It is likely that the following mechanism proposed by Rüchardt and Merz[11] for the Gomberg reaction is also

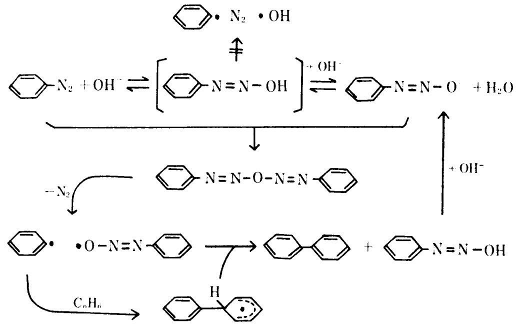

TABLE 2. ORIENTATION (%) AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH PhN_2BF_4 IN THE PRESENCE OF $(CH_3)_4N^+OH^-$ IN H_2O AT 20°C

X in PhX	Orientation (%)			Partial rate factors		
	o-,	*m*-,	*p*-,	k_o/k	k_m/k	k_p/k
-OMe	70.5	18.8	10.7	4.36	1.14	1.31
-Et	53.3	28.1	18.6	1.69	0.90	1.17
-Cl	63.1	19.7	17.2	3.21	1.02	1.76
-CN	65.4	13.3	21.3	11.9	2.43	7.77
$-NO_2$	64.0	9.1	26.9	13.9	1.83	11.2

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8) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960), p. 73.

9) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

10) M. Kobayashi, H. Minato, and N. Kobori, This Bulletin, **43**, 219 (1970).

11) C. Rüchardt and E. Merz, *Tetrahedron Lett.*, **1964**, 2431.

TABLE 3. ρ_p VALUES[a] FOR THE PHENYLATION WITH PHENYL RADICALS

Exp. No.	Source of Ph·	Solvent	Temp. (°C)	H-Abstractor	ρ_p
1	PhN_2BF_4-$Me_4N^+OH^-$	Aromatics-DMSO	20	Ph-N=N-O·	1.69[b]
2	PhN_2BF_4-$NaNO_2$	Aromatics-DMSO	20	Ph-N=N-O· or NO_2	1.67[c]
3	PhN_2BF_4-Choline	Aromatics-DMSO	20	Ph-N=N-O·	1.63[b]
4	PhN_2BF_4-$Me_4N^+OH^-$	Aromatics-H_2O	20	Ph-N=N-O·	1.38[b]
5	$PhN(NO)COCH_3$	Aromatics	20	Ph-N=N-O· or Ph-N-O· Ph-$\overset{\vert}{\text{N}}$-$COCH_3$	1.27[d]
6	$(PhCO_2)_2$	Aromatics	80	BPO or disproportionation	1.15[e]
7	PhN=N-CPh_3	Aromatics-DMSO	60	Ph_3C·	0.93[f]

a) ρ Values for the reaction reported in the literature were calculated by ploting the observed *para* partial rate factors against σ_p. b) this work, c) Ref. 5, d) Ref. 9, e) Ref. 8, f) to be published

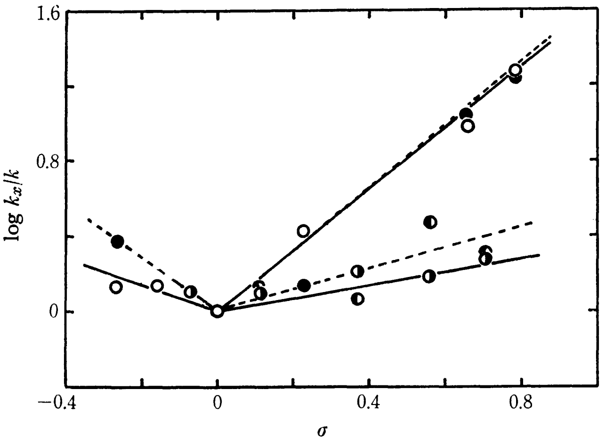

Fig. 1. The Hammett plots for the phenylation of PhX with PhN_2BF_4 in DMSO at 20°C.

—◑—◑— log k_m/k, ρ_m=0.34 } with choline
—○—○— log k_p/k, ρ_p=1.63 } with choline
---◐---◐--- log k_m/k, ρ_m=0.48 } with $(CH_3)_4N^+OH^-$
---●---●--- log k_p/k, ρ_p=1.69 } with $(CH_3)_4N^+OH^-$

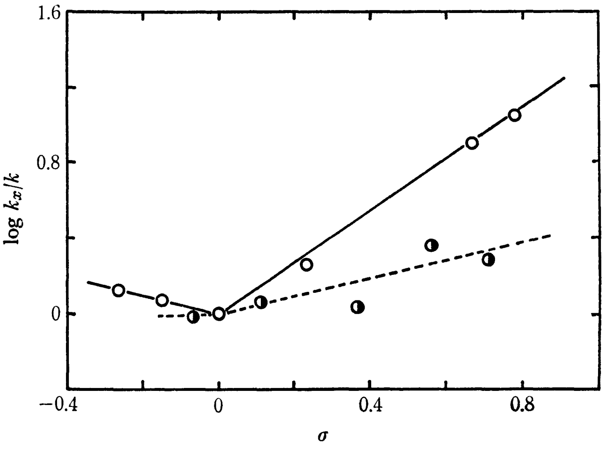

Fig. 2. The Hammett plots for the phenylation of PhX with PhN_2BF_4 in the presence of $(CH_3)_4N^+OH^-$ in H_2O.

---◑---◑--- log k_m/k, ρ_m=0.46
—○—○— log k_p/k, ρ_p=1.38

applicable to the homogeneous reaction between PhN_2^+-BF_4^- and $R_4N^+OH^-$ in DMSO.

Although the Gomberg reaction has been used extensively for synthetic purposes, the partial rate factors for phenylation of substituted benzenes by the Gomberg reaction have not been determined yet. Therefore, the partial rate factors and orientation were determined under the ordinary Gomberg reaction conditions (*i. e.*, heterogeneous mixtures of aromatics and water) using tetramethylammonium hydroxide as a strong base instead of sodium hydroxide commonly used. The results are shown in Table 2.

Figures 1 and 2 are the Hammett's plots of the partial rate factors of the *meta* and *para* positions. Satisfactory V-shape relationships are observed for *meta* and *para* data with ρ_m=0.34, ρ_p=1.63 (with choline, in DMSO), ρ_m=0.48, ρ_p=1.69 (with tetramethylammonium hydroxide, in DMSO) and ρ_m=0.46, ρ_p=1.38 (with tetramethylammonium hydroxide, in H_2O). The ρ values were calculated from the right half of the V-shape which contained larger number of experimental data than the left half.

Table 3 summarized the ρ_p values for the phenylation under various reaction conditions. It is interesting to compare the ρ_p values in Table 3. In PhN_2BF_4–$NaNO_2$, -Choline, and -Me_4NOH in DMSO, the ρ_p values are in the range of 1.63–1.69. The smaller ρ value (1.38) observed in PhN_2BF_4—Me_4NOH in H_2O may be ascribed to the change in solvents. In these four systems, the hydrogen abstractor is probably the same, *i.e.*, Ph–N=N–O·.

In three other systems listed in Table 3, the ρ_p values are much smaller. If the hydrogen abstractor in *N*-nitrosoacetanilide is Ph–N=N–O·, the smaller ρ_p value (1.27) compared with those in Expt. 1—3, must be ascribed to the difference in solvents. However, if the hydrogen abstractor in this system is Ph–N–O·
Ph–$\overset{\vert}{\text{N}}$–$COCH_3$
as Chalfont and Perkins proposed,[12] the smaller ρ value can be ascribed to the difference in solvents and hydrogen abstractors.

In benzoyl peroxide and phenylazotriphenylmethane the temperatures are higher (80 and 60°C), and it is likely that reactions are less selective and ρ values are smaller at higher temperatures. The hydrogen abstractor in these systems are also different from those in Expts. 1—4.

Clear interpretation of these different ρ values, however, can be made only after more detailed studies are carried out.

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[12] C. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, **89**, 3054 (1967).