BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 215—219 (1970)

# Cationic Arylation. I. Phenylation of Substituted Benzenes with Benzenediazonium Tetrafluoroborate in Homogeneous Solution

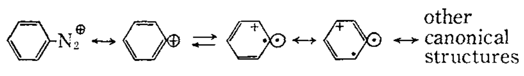
Michio KOBAYASHI, Hiroshi MINATO, Eiichi YAMADA and Nobumasa KOBORI

*Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo*

(Received June 27, 1969)

Substituted benzenes were phenylated with benzenediazonium tetrafluoroborate in homogeneous solutions with DMSO or acetonitrile. The distribution of substituted biphenyls and the partial rate factors indicated that this phenylation was an electrophilic substitution, but the selectivity was much smaller than those of nitration or sulfonylation. Experiments with chlorobenzene-4*d*, anisole-4*d* and chlorobenzene-$d_5$ showed that both the orientation and partial rate factors did not change with deuterated compounds. Therefore, it was established that the rate-determining step was the addition of phenyl cation to an aromatic nucleus, and not the abstraction of proton from the phenylated intermediate.

Abramovitch and Saha[1] studied the arylation of aromatic compounds with benzenediazonium tetrafluoroborate, and on the basis of the isomer ratios and the apparent total rate ratios they suggested that the phenyl cation initially formed isomerized to a diradical cation.



[I] [IIa] [IIb]

However, the reaction was carried out in heterogeneous media and there was no kinetic control in the reaction conditions. An investigation of this reaction in homogeneous media seemed desirable.

Recently Abramovitch and Gadallah[2] reported the results of the phenylation in mixtures of substituted benzenes and acetonitrile or sulpholan. This prompted us to report on our findings in the phenylation in homogeneous solutions consisting of aromatic solvents and dimethyl sulfoxide (DMSO) or acetonitrile. On the basis of the partial rate factors of substituted benzenes and substituted deuterated benzenes in homogeneous solution the mechanism of the phenylation with benzenediazonium tetrafluoroborate will be discussed.

## Experimental

**Materials.** Dimethyl sulfoxide and acetonitrile were purified according to the methods described in a previous paper.[3] Benzene, toluene, ethylbenzene and chrolobenzene were washed with concentrated sulfuric acid and water successively, dried over calcium chloride, and distilled. Boiling points were 80°C, 110°C, 135.7°C and 131°C, respectively. Anisole was washed with an aqueous sodium hydroxide solution and water, dried over calcium chloride, and distilled; bp 153°C. Methyl benzoate was prepared from benzoic acids and methanol, washed with water, dried over magnesium sulfate, and then fractionally distilled; bp 110°C/50 mmHg. Nitrobenzene was washed repeatedly with a potassium dichromate solution, dried over calcium chloride, and distilled; bp 95.5°C/18 mmHg.

Benzenediazonium tetrafluoroborate was prepared according to the method decribed previously.[3]

Isomeric methylbiphenyls, ethylbiphenyls, methoxybiphenyls, chlorobiphenyls, methoxycarbonylbiphenyls and nitrobiphenyls were prepared as the reference compounds by the methods described in literature.[4] They were purified by elution chromatography, distillation or recrystallization, and their melting points and boiling points agreed with the values in literature. Dibenzyl and $\beta$-methoxynaphthalene were purified by recrystallization.

Anisole-4*d* was prepared by the hydrolysis of *p*-methoxyphenylmagnesium bromide in $D_2O$ (isotopic purity, 99.75%, supplied by E. Merck AG, Darmstadt); bp 58°C/15 mmHg. Its isotopic purity was determined to be 92% by mass spectrometry using Hitachi RMU-6B. Chlorobenzene-4d was prepared by the same method from *p*-bromochlorobenzene; bp 131°C. Its isotopic purity was found to be 90%.

Chlorobenzene-$d_5$ of CIBA Limited was used without further purification. Guaranteed isotopic purity was 99.6%.

**Decomposition of Benzenediazonium Tetrafluoroborate.** In 20.0 g of dimethyl sulfoxide (DMSO) or acetonitrile 2.0 g of benzenediazonium tetrafluoroborate was dissolved, and the solution was diluted with substituted benzenes (the molar ratio of substituted benzene *versus* the diazonium salts was 50). The homogeneous solution was placed in a bath at 40±0.1°C, and the decomposition was followed by measuring the rate of evolution of nitrogen. After the evolution of nitrogen ceased, the reaction mixture was washed with water to remove the polar solvent, washed with a 5% sodium hydroxide solution to remove acidic products, washed with water, dried over magnesium sulfate, and then the amounts of substituted biphenyl isomers were determined by a Hitachi Gas Chromatograph K-53.

Since the presence of a large quantity of substituted benzenes made the gas chromatographic determination of substituted biphenyls unreliable because of tailing, the determination was carried out after about 80% of substituted benzenes had been evaporated. Chlorobenzene was chosen as the standard for competitive experiments since non-substituted biphenyl easily sublimes. The biphenyl isomers were identified by comparison of their retention times with those of authentic samples, and their amounts were determined by use of calibration curves. Columns used were packed with Apiezon L (10%) on Chromosorb W, and their lengths varied from 1 m to 6 m depending on the ease of separation of isomers.

## Results and Discussion

Decomposition of benzenediazonium tetrafluoroborate in homogeneous mixtures of substituted

Table 1. First order rate constants for the decomposition of $PhN_2BF_4$ in homogeneous solution at 40°C

| Solvents | $10^4 k_1$ (sec$^{-1}$) |
|---|---|
| DMSO-PhH-PhCl | 3.82 |
| DMSO-PhH-$PhCH_3$ | 3.81 |
| DMSO-PhCl-$PhOCH_3$ | 3.82 |
| DMSO-PhCl-$PhNO_2$ | 3.62 |
| DMSO-PhH-$PhC_2H_5$ | 3.84 |
| DMSO-PhH-$PhCO_2CH_3$ | 4.06* |
| DMSO only | 3.89 |
| $CH_3CN$-PhH-$PhC_2H_5$ | 3.25 |
| $CH_3CN$-PhH-PhCl | 3.10 |
| $CH_3CN$-PhCl-$PhOCH_3$ | 3.48 |
| $CH_3CN$-PhCl-$PhNO_2$ | 3.44 |
| $CH_3CN$-PhH-$PhCO_2CH_3$ | 3.19 |
| $CH_3CN$ only | 3.15** |

* at 40.2°C, ** at 39.8°C

---

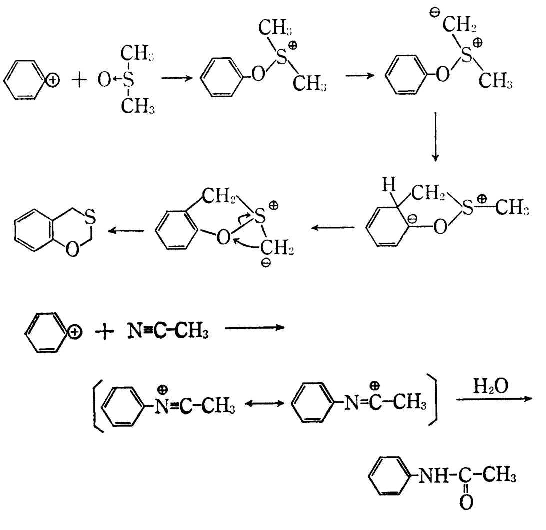
1) R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965).

2) R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc.*, *B*, **1968**, 497.

3) R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., London (1957); P. E. Fanta, *Chem. Rev.*, **64**, 613 (1964); M. Kobayashi, E. Yamada, M. Matsui and N. Kobori, *Organic Preparations and Procedures*, in press.

benzenes-DMSO and substituted benzenes-acetonitrile was of first order, and the rate constants are shown in Table 1. The average value of first-order rate constants in DMSO-$C_6H_5X$ was $3.84\times10^{-4}$ ($sec^{-1}$) and that in $CH_3CN$-$C_6H_5X$ was $3.27\times10^{-4}$ ($sec^{-1}$), which were approximately the same as those in pure DMSO and in pure acetonitrile. This shows that benzenediazonium tetrafluoroborate decomposes in these solvent systems to produce phenyl cation and nitrogen gas under the same mechanism.

As products other than substituted biphenyls, 1,3-benzoxathiane (about 8 mol%) was obtained from the reactions in DMSO-$C_6H_5X$, and acetanilide (about 50 mol%) was obtained from the reactions in $CH_3CN$-$C_6H_5X$. Products of dimerization or disproportionation were not found. Apparently the electron-rich oxygen atom of DMSO and nitrogen atom of acetonitrile compete with the aromatic nucleus in reaction with the electrophilic phenyl cation as follows.



Because of these reactions, yields of biphenyls are not so high; 7% in $PhNO_2$-DMSO, 12.4% in PhCl-DMSO, and 20.8% in PhOMe-DMSO.

Orientation for phenylation with benzenediazonium tetrafluoroborate in PhX-DMSO and in PhX-$CH_3CN$ is summarized in Table 2. Benzenes substituted with methoxy, methyl, ethyl and chloro groups are *o,p*-directors, and benzenes substituted with methoxycarbonyl and nitro groups are *m*-directors. This indicates that the reactions are of electrophilic nature. Except for nitrobenzene, more *ortho* and *para* isomers were produced in $CH_3CN$-PhX than in DMSO-PhX, and especially the amounts of *ortho* isomers were greater. These results are in contrast with the findings that greater amounts of *ortho* isomers were produced in DMSO-PhX than in $CH_3CN$-PhX by free radical phenylation with phenylazotriphenylmethane.[4]

TABLE 2. ORIENTATION (%) FOR THE PHENYLATION OF PhX WITH $PhN_2BF_4$ IN HOMOGENEOUS SOLUTION AT 40°C

| PhX | In DMSO | | | In $CH_3CN$ | | |
|---|---|---|---|---|---|---|
| | *o*- | *m*- | *p*- | *o*- | *m*- | *p*- |
| $OCH_3$ | 56.4 | 12.2 | 31.4 | 64.0 | 8.5 | 27.5 |
| | 56.0 | 12.2 | 31.8 | 65.6 | 8.2 | 26.2 |
| $CH_3$ | 47.3 | 21.1 | 31.6 | | | |
| | 47.1 | 20.9 | 32.0 | | | |
| $C_2H_5$ | 46.2 | 29.3 | 24.6 | 50.4 | 25.8 | 23.8 |
| | 42.9 | 29.8 | 27.3 | 49.3 | 25.2 | 25.5 |
| Cl | 48.2 | 24.0 | 27.8 | 61.5 | 15.7 | 22.8 |
| | 49.8 | 22.8 | 27.4 | 61.5 | 14.3 | 23.8 |
| | 44.1* | 26.1* | 29.8* | | | |
| $CO_2CH_3$ | 43.1 | 43.5 | 13.4 | 53.4 | 36.5 | 10.1 |
| | 46.1 | 42.1 | 11.8 | 52.5 | 37.5 | 10.0 |
| $NO_2$ | 38.1 | 48.4 | 13.5 | 29.5 | 48.2 | 22.3 |
| | 36.4 | 50.3 | 13.3 | 31.8 | 52.0 | 16.2 |

* reaction carried out in oxygen atmosphere

TABLE 3. PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH $PhN_2BF_4$ IN HOMOGENEOUS SOLUTION AT 40°C

| PhX | In DMSO | | | In $CH_3CN$ | | |
|---|---|---|---|---|---|---|
| | $k_o/k$ | $k_m/k$ | $k_p/k$ | $k_o/k$ | $k_m/k$ | $k_p/k$ |
| $OCH_3$ | 3.14 | 0.68 | 3.50 | 1.74 | 0.23 | 1.49 |
| | 3.14 | 0.68 | 3.57 | 1.80 | 0.22 | 1.44 |
| $CH_3$ | 1.32 | 0.61 | 1.84 | | | |
| | 1.35 | 0.60 | 1.84 | | | |
| $C_2H_5$ | 1.31 | 0.83 | 1.40 | 1.51 | 0.77 | 1.43 |
| | 1.31 | 0.91 | 1.67 | 1.39 | 0.71 | 1.44 |
| Cl | 1.02 | 0.51 | 1.17 | 0.67 | 0.17 | 0.49 |
| | 1.03 | 0.47 | 1.13 | 0.67 | 0.16 | 0.62 |
| | 1.01* | 0.60* | 1.37* | | | |
| $CO_2CH_3$ | 0.40 | 0.40 | 0.25 | 0.54 | 0.37 | 0.20 |
| | 0.44 | 0.40 | 0.22 | 0.57 | 0.41 | 0.22 |
| $NO_2$ | 0.29 | 0.37 | 0.21 | 0.10 | 0.16 | 0.15 |
| | 0.29 | 0.40 | 0.21 | 0.09 | 0.14 | 0.09 |

* reaction carried out in oxygen atmosphere

Table 3 shows the partial rate factors calculated on the assumption that the step of σ-complex formation is rate-determining. Differences between the values in DMSO-PhX and those in $CH_3CN$-PhX may be ascribed to the difference in the solvation of the transition states and aryl cations. Variations in the partial rate factors in Table 3 are consistent with the electrophilic nature of the reactions except that the selectivity is very small

---

[4] M. Kobayashi, H. Minato, N. Watanabe and N. Kobori, This Bulletin, **43**, 258 (1970).

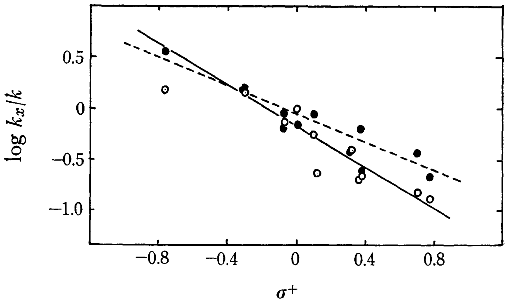


Fig. 1. The Hammett plots for the phenylation of PhX with $PhN_2BF_4$.
—○—: in $CH_3CN$, $\rho = -0.82$, $r = 0.91$
---●---: in DMSO, $\rho = -0.74$, $r = 0.93$

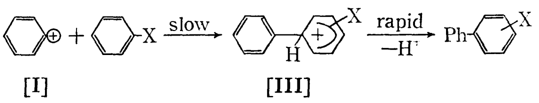
compared with that in nitration⁵⁾ or sulfonylation⁶⁾ of aromatic compounds. However, the selectivity or the partial rate factors for phenylation with phenyl cation are quite different from those of phenylation with phenyl radical.

log $k_m/k$ or log $k_p/k$ is better correlated with $\sigma^+$ of Brown-Okamoto than $\sigma$ values Hammett, as shown in Fig. 1. However, the correlation is not so good, and the correlation coefficient is 0.93 in DMSO-PhX and 0.91 in $CH_3CN$-PhX. The reaction constant, $\rho$, is small compared with that in ordinary ionic reactions (−0.74 in DMSO-PhX and −0.82 in $CH_3CN$-PhX), but the fact that it is negative indicates that these reactions are electrophilic and are different from phenylation with phenyl radical.⁷˒⁸⁾ Various features of phenylation with phenyl cation are best explained on the assumption that the phenyl cation initially formed isomerizes to a diradical cation [II] with concerted uncoupling of a pair of $\pi$-electrons, one of which falls into the vacant $sp^2$ $\sigma$-orbital.¹˒⁹⁾

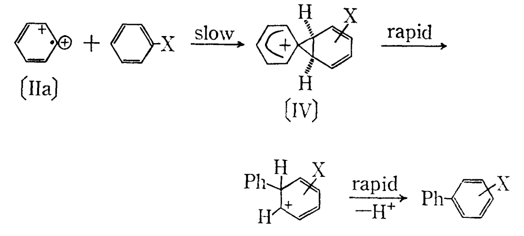
Under an oxygen atmosphere yields of phenylation with phenyl radical greatly decrease, whereas those with phenyl cation do not change, as shown by the data with chlorobenzene in Tables 2 and 3. This finding is not inconsistent with the biradical nature of phenyl cation, since the non-reactivity is ascribable to the repulsion between the strongly electrophilic oxygen and the strongly electrophilic phenyl cation.

Abramovitch and Gadallah²⁾ did not attempt to correlate the partial rate factors with $\sigma^+$ or $\sigma$. If their values are plotted *versus* $\sigma^+$, $\rho$ is −0.66 at 65°C with the correlation coefficient of 0.96. This $\rho$ value is consistent with the value reported in this paper if the difference in the temperatures is taken into consideration.

The correlation in the Hammett plots of our data as well as the data of Abramovitch and Gadallah²⁾ is much worse than that of ordinary ionic reactions. In an attempt to explain the apparent slight deactivation of the *meta*-position in toluene towards phenylation in $CH_3CN$-PhMe at 65°C ($k_m/k = 0.85$), Abramovitch and Gadallah²⁾ suggested that the rate-determining step in these reactions was not the formation of $\sigma$-complex [III] *via* Scheme 1, but the addition of IIa to a benzene double bond to form the various possible spirocyclopropane phenonium ions [IV], followed by ring-opening to give the three substituted $\sigma$-complexes in a product-, but not rate-, determining step.



Scheme 1



Scheme 2

Our data show considerable deactivation of the *meta* position in toluene($k_m/k = 0.60$ in DMSO-PhMe) and in ethylbenzene ($k_m/k = 0.74$ in $CH_3CN$-PhEt and 0.87 in DMSO-PhEt), and these values are in line with their suggestion.

In an attempt to elucidate the mechanism of this phenylation further, isotope effects were examined by use of anisole-4*d*, chlorobenzene-4*d* and chlorobenzene-$d_5$. The results are shown in Table 4. When anisole-4*d* or chlorobenzene-4*d* was phenylated with benzenediazonium tetrafluoroborate in a mixture with DMSO, the distributions of isomeric biphenyls were approximately the same as those with anisole or chlorobenzene. When

Table 4. Phenylation of deuterated PhX with $PhN_2BF_4$ in DMSO at 40°C

| PhX | Orientation (%) | | | Partial rate factors | | |
|---|---|---|---|---|---|---|
| | *o*- | *m*- | *p*- | $k_o/k$ | $k_m/k$ | $k_p/k$ |
| $PhOCH_3$-4*d* | 54.8 | 13.5 | 31.7 | | | |
| ($PhOCH_3$) | 56.2 | 12.2 | 31.6 | | | |
| PhCl-4*d* | 44.0 | 23.9 | 32.1 | | | |
| (PhCl) | 45.7 | 21.6 | 32.7 | 1.02 | 0.49 | 1.15 |
| PhCl-$d_5$ | 43.8 | 25.3 | 30.9 | 0.89 | 0.52 | 1.26 |

---

5) L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **81**, 3323 (1959).

6) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 4046 (1958).

7) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London (1960).

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

9) R. W. Taft, *J. Amer. Chem. Soc.*, **83**, 3350 (1961).

a mixture of chlorobenzene-$d_5$ and benzene was phenylated and the partial rate factors were calculated, the values of $k_H/k_D$ for *ortho*, *meta* and *para* were approximately 1 within experimental error of gas chromatography. These findings show that in phenylation with phenyl cation there is no isotope effect as in the cases of nitration and free radical arylation[10] of aromatic compounds.

So far there is no conclusive evidence which enables us to choose Scheme 1 or Scheme 2 as the mechanism of the phenylation with phenyl cation. However, it has been established that the rate-determining step is the addition of the phenyl cation to an aromatic nucleus, and not the abstraction of proton from the phenylated intermediate.

---

10) E. L. Eliel, S. Meyerson, Z. Welvart and S. H. Wilen, *ibid.*, **82**, 2936 (1960).