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# Aromatic Arylation with Aryl Radicals. I. A Novel Method for Generating Aryl Free Radical

Michio Kobayashi, Hiroshi Minato, Nobumasa Kobori and Eiichi Yamada

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

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Benzenediazonium tetrafluoroborate in DMSO decomposed instantaneously with evolution of nitrogen upon addition of a DMSO solution of sodium nitrite. Orientations and partial rate factors for phenylation of substituted benzenes indicated that not phenyl cation but phenyl radical was produced as an intermediate. Hammett's plots of partial rate factors of meta and para positions yielded good straight lines with $\rho_m = 0.46$ and $\rho_p = 1.67$. Plausible mechanisms were discussed. From *m*-dinitrobenzene 2,6- and 2,4-dinitrobiphenyl were produced in 47 and 23% yields, respectively, and the synthetic value of this method was pointed out.

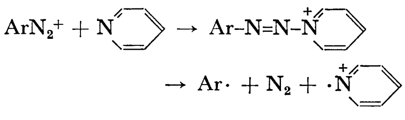
Aryldiazonium salts decompose with evolution of nitrogen in aprotic polar solvents, and phenyl cation is considered to be the intermediate on the basis of the kinetic studies[1] and the partial rate factors for arylation of substituted benzenes.[2]

$$ArN_2^+ \rightarrow Ar^+ + N_2$$

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

$$ArN_2^+ + CH_3O^- \rightarrow Ar\text{–}N\text{=}N\text{–}OCH_3$$
$$\rightarrow Ar\cdot + N_2 + \cdot OCH_3$$

or



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[1] E. S. Lewis, *J. Amer. Chem. Soc.*, **80**, 1371 (1958); 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).

During a systematic investigation on the decomposition of aryldiazonium salts in aprotic polar solvents in our laboratories, it has been found that aryldiazonium salts decompose instantaneously with evolution of nitrogen upon addition of sodium nitrite in dimethyl sulfoxide (DMSO) at room temperature. In this paper, the results of this investigation will be described, and the evidence for the homolytic nature of the decomposition will be presented. Synthetic utility of this reaction will be also pointed out.

## Experimental

**Materials.** Preparation of benzenediazonium tetrafluoroborate and substituted biphenyls, and purification of DMSO and substituted benzenes were described in our previous paper.[2b] *m*-Dinitrobenzene, *p*-nitrotoluene, *p*-chloronitrobenzene, 1,3,5-trinitrobenzene and sodium nitrite were the first grade chemicals of Wako Pure Chemical Industries, and were used without further purification.

**Phenylation of Monosubstituted Benzenes.** Under nitrogen atmosphere a solution of 2.00 g of benzenediazonium tetrafluoroborate in 20 g of DMSO was added drop by drop at 10°C into a vigorously stirred solution of sodium nitrite (3 mol/mol of $PhN_2BF_4$) and a substituted benzene (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 sodium nitrite. After it was dried over magnesium sulfate, ether and about 70% of the remaining substituted benzene was evaporated, and biphenyl isomers in the residue was analyzed by 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 non-substituted biphenyl easily sublimes and the evaporation of a remaining substituted benzene will bring forth a great error. The reactivity of each position of substituted benzenes was calculated relative to the reactivity of the ortho position of chlorobenzene. A competitive phenylation between benzene and chlorobenzene was carried out without evaporation in order to determine the partial rate factor of the ortho position of chlorobenzene. The partial rate factors of various substituted benzenes were calculated by the following equation.

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

**Phenylation of Poly-substituted Benzenes.** The experimental procedure was the same as that described for mono-substituted benzenes except where otherwise stated.

***p*-Nitrotoluene.** A solution of *p*-nitrotoluene (10.0 g) and sodium nitrite (2.5 g) in DMSO (30 g) was added to a stirred solution of benzenediazonium tetrafluoroborate (3.717 g) in DMSO (30 g). Biphenyl isomers were separated by a gas chromatograph, and the fractions isolated were identified by infrared spectroscopy, NMR spectroscopy (in $CDCl_3$) and elemental analyses, and quantitative determinations were made by gas chromatography. 3-Methyl-6-nitrobiphenyl. $H^2$: 2.64 $\tau$ (singlet); $H^4$: 2.71 $\tau$ (doublet, $J_{45}=9.0$ Hz); $H^5$: 2.20 $\tau$ (doublet, $J_{54}=9.0$ Hz). Found: C, 73.75; H, 5.72%. Calcd for $C_{13}H_{11}O_2N$: C, 73.22; H, 5.20%. 2-Methyl-5-nitrobiphenyl. $H^3$: 2.76 $\tau$ (multiplet); $H^4$ and $H^6$: 1.90 $\tau$ (multiplet). Found: C, 73.46; H, 5.50%. Calcd for $C_{13}H_{11}O_2N$: C, 73.22; H, 5.20%.

***p*-Nitrochlorobenzene.** A solution of *p*-nitrochlorobenzene (16.0 g) and sodium nitrite (4.0 g) in DMSO (30 g) was added to a stirred solution of benzenediazonium tetrafluoroborate (3.445 g) in DMSO (20 g). Biphenyl isomers were separated by a gas chromatograph, and the fractions isolated were identified by infrared spectroscopy, NMR spectroscopy (in $CDCl_3$) and elemental analyses, and determined quantitatively by gas chromatography. 3-Chloro-6-nitrobiphenyl. $H^2$: 2.24 $\tau$ (singlet); $H^4$: 2.55 $\tau$ (doublet, $J_{45}=9.0$ Hz); $H^5$: 2.16 $\tau$ (doublet, $J_{54}=9.0$ Hz). Found: C, 61.29; H, 3.46%. Calcd for $C_{12}H_8O_2NCl$: C, 61.69; H, 3.45%. 2-Chloro-5-nitrobiphenyl. $H^3$: 2.37 $\tau$ (doublet, $J_{34}=9.0$ Hz); $H^4$: 1.86 $\tau$ (doublet, $J_{43}=9.0$ Hz); $H^6$: 1.77 $\tau$ (singlet). Found: C, 61.9; H, 3.14%. Calcd for $C_{12}H_8O_2NCl$: C, 61.69; H, 3.45%.

***m*-Dinitrobenzene.** A solution of *m*-dinitrobenzene (10.0 g) and sodium nitrite (5.0 g) in DMSO (22 g) was added to a stirred solution of benzenediazonium tetrafluoroborate (4.237 g) in DMSO (10 g). Chloroform instead of ether was used for extraction. Substituted biphenyl isomers were separated on an alumina column with hexane-benzene as the eluant, and recrystallized from ethyl acetate. 2,4-Dinitrobiphenyl, 2.1 g (47%), mp 108°C (lit,[5] 110°C). 2,6-Dinitrobiphenyl, 1.1 g (23%), mp 186—187°C (lit,[6] 188—189°C).

**1,3,5-Trinitrobenzene.** A solution of 1,3,5-trinitrobenzene (4.0 g) and sodium nitrite (5.0 g) in DMSO (30 g) was added to a stirred solution of benzenediazonium tetrafluoroborate (4.50 g) in DMSO (10 g). Chloroform was used for extraction. 2,4,6-Trinitrobiphenyl was isolated by elution chromatography on a silica gel column with hexane-benzene as the eluant; 2.55 g (55%), mp 129°C (lit, 130°C).[5]

## Results and Discussion

Benzenediazonium tetrafluoroborate in DMSO decomposed instantaneously with evolution of nitrogen upon addition of a DMSO solution of sodium nitrite. Since in the absence of sodium nitrite the diazonium salts slowly undergoes a first-order decomposition *via* phenyl cation,[2b] the mechanism of this rapid decomposition must be different from that involving phenyl cation. The difference of the mechanism is also suggested from the absence of 1,3-benzoxathian in the products, which was always produced when phenyl

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5) H. C. Gull and E. E. Turner, *J. Chem. Soc.*, **1929**, 491.

6) J. Forrest, *ibid.*, **1960**, 566.

Table 1. Orientation and partial rate factors for the phenylation of PhX with $PhN_2BF_4$ in DMSO in the presence of $NaNO_2$ at room temperature

| PhX | Yield[a] (%) | Orientation (%) | | | Partial rate factors | | |
|---|---|---|---|---|---|---|---|
| | | o- | m- | p- | $k_o/k$ | $k_m/k$ | $k_p/k$ |
| $PhOCH_3$ | — | 72.4 | 14.2 | 13.4 | 5.66 | 1.11 | 2.09 |
| $PhC_2H_5$ | — | 49.8 | 32.9 | 17.3 | 2.49 | 1.64 | 1.73 |
| PhCl | 22.6 | 58.8 | 25.4 | 15.8 | 3.89 | 1.68 | 2.09 |
| PhCl | 18.5 | 57.1 | 25.4 | 17.5 | 3.24 | 1.44 | 1.98 |
| PhCl[b] | 15.6 | 56.8 | 24.7 | 18.5 | 3.51 | 1.53 | 2.29 |
| $PhCO_2CH_3$ | — | 32.4 | 20.2 | 47.4 | 1.90 | 1.19 | 5.57 |
| PhCN | — | 46.5 | 13.7 | 39.8 | 5.71 | 1.68 | 9.80 |
| $PhNO_2$ | 76.3 | 67.8 | 5.4 | 26.9 | 26.6 | 2.12 | 21.1 |

a) Mole percent per mole diazonium salt.
b) Reaction was carried out in water under heterogeneous conditions.

cation was generated in DMSO.[2b]

Table 1 shows the orientations and partial rate factors for phenylation of substituted benzenes with benzenediazonium tetrafluoroborate and sodium nitrite in DMSO. All the substituents behaved as *o,p*-directors, and partial rate factors were always larger than 1. These data are similar to those of phenylation with phenyl radical produced from benzoyl peroxide[7a] or *N*-nitrosoacetanilide[7b] and quite different from those of phenylation with phenyl cation.[2,8] These findings indicate that the benzenediazonium salt reacts with sodium nitrite and produces phenyl radical. Plausible mechanisms are the following two.

$PhN_2^+ + {}^-O\text{-}N{=}O \rightarrow Ph\text{-}N{=}N\text{-}O\text{-}N{=}O$
(I)

Scheme 1

$Ph\text{-}N{=}N\text{-}O\text{-}N{=}O \rightarrow Ph\cdot + N_2 + NO_2$

Scheme 2

$2Ph\text{-}N{=}N\text{-}O\text{-}N{=}O \rightarrow Ph\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ph + N_2O_3$
(II)

$Ph\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ph \rightarrow Ph\cdot + N_2 + Ph\text{-}N{=}N\text{-}O\cdot$

Since $NO_2$ and PhN=NO· are rather stable radicals, it is possible that compound I or II decomposes quickly as they are formed.

It is generally recognized that excess sodium nitrite should not be present when aryldiazonium salts are prepared, but no satisfactory explanation for the harmful action of nitrites has been proposed yet. The results of this investigation show that the excess nitrite not only decompose the aryldiazonium salts but also produce very reactive phenyl radical, which attacks various compounds present in the medium, producing a mixture of complicated products.

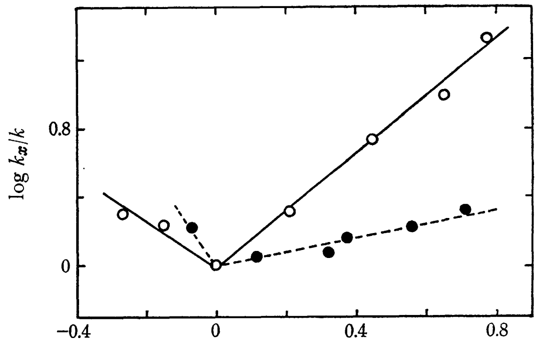

Fig. 1. The Hammett' plots for the phenylation with $PhN_2BF_4NaNO_2$ in DMSO.
---●---: log$k_m/k$, $\rho_m$=0.46
—○—: log$k_p/k$, $\rho_p$=1.67

Figure 1 is the Hammett's plots of partial rate factors of meta and para positions. Satisfactory linear relationships of V-shape are observed for meta and para data with $\rho_m=0.46$ and $\rho_p=1.67$. $\rho$ Values were calculated from the right half of the V-shape which contained larger number of experimental data than the left half. Figure 2 shows

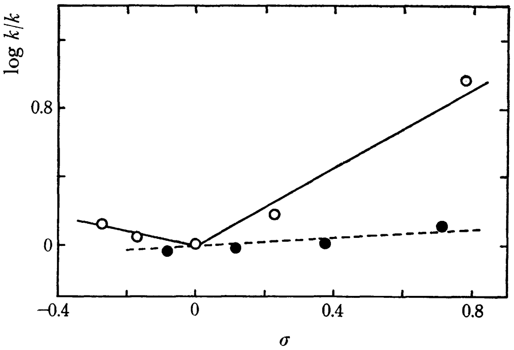

Fig. 2. The Hammett' plots for the phenylation with $PhN(NO)COCH_3$ at 20°C.
---●---: log$k_m/k$, $\rho_m$=0.07
—○—: log$k_p/k$, $\rho_p$=1.27

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7) a) G. H. Willlams "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960), p. 73. b) R. Ito, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

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

the Hammett's plots of partial rate factors obtained by Ito, Migita, Morikawa and Simamura[7b] for phenylation with *N*-nitrosoacetanilide (without consideration of the conjugative effect $\tau_p$). It is a satisfactory linear relationship of V-shape with $\rho_m=0.07$ and $\rho_p=1.27$. Both $\rho_m$ and $\rho_p$ of this investigation were greater than those of *N*-nitrosoacetanilide. The difference might be ascribed to solvent effect, *i.e.*, the use of the polar solvent, DMSO, in this investigation. However, it has been found in our laboratories that the $\rho$ value for the partial rate factors for phenylation with phenyl radical generated from phenylazotriphenylmethane in PhX-DMSO is not greater than that in PhX alone,[9] and this finding shows that the greater $\rho$ value in this investigation is not due to solvent effect. Since sodium nitrite is insoluble in less polar organic solvents, it is not possible to investigate the reaction between benzenediazonium tetrafluoroborate and sodium nitrite in other solvents.

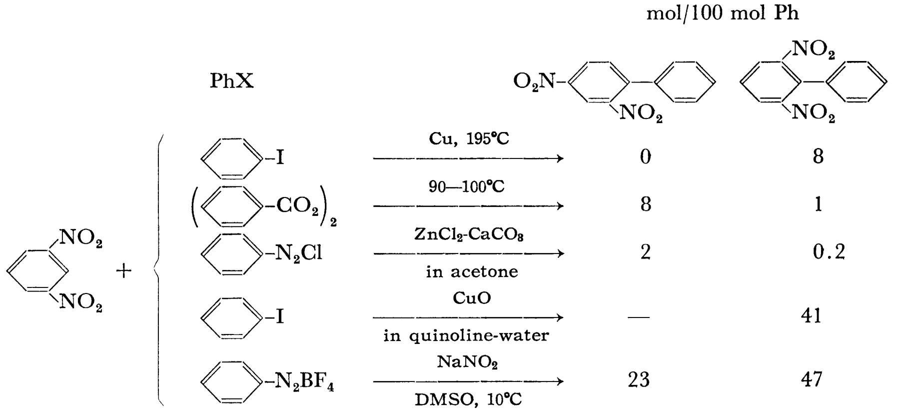
The greater $\rho$ values may be ascribed to the difference in the species abstracting hydrogen from the intermediate phenylcyclohexadienyl radicals. The hydrogen abstractor in Scheme 1 is $NO_2$, and that in Scheme 2 is PhN=N-O• or $N_2O_3$. As for the hydrogen abstractor for *N*-nitrosoacetanilide, Ruchardt and his coworkers reported that PhN=NO• is the species which abstracts hydrogen,[10] whereas Chalfont and Perkins reported that Ph(Ac)N-(Ph)N-O• abstracts hydrogen.[11] If the hydrogen abstractor in the case of *N*-nitrosoacetanilide is Ph(Ac)N-(Ph)N-I•, the difference in the $\rho$ values may be ascribed to the difference in the hydrogen-abstracting species. If the hydrogen abstractor in the case of *N*-nitrosoacetanilide is is PhN=N-O•, the difference in the $\rho$ values can be ascribed to the difference in the hydrogen-abstracting species only when the hydrogen abstractor in the $PhN_2BF_4$-$NaNO_2$ system is $NO_2$ or $N_2O_3$, and not PhN=N-O•. At present it is not possible to determine what the true hydrogen abstractor in this system is. In our laboratories phenylation with phenylazotriphenylmethane in the presence of $N_2O_4$ is being investigated and the capacity of $N_2O_4$ as a hydrogen abstractor is being examined.[9]

It is interesting to note that the values of $\rho_p-\rho_m$ are approximately the same in both cases ($1.27-0.07=1.20$ for *N*-nitrosoacetanilide and $1.67-0.46=1.21$ for $PhN_2BF_4$-$NaNO_2$). This fact seems to indicate that the contributions of the direct conjugative effect of *p*-substituents are similar in both cases.

Table 1 shows that the yield of phenylation of nitrobenzene is 76.3%, which is much better than those of chlorobenzene. Williams and his coworkers observed that in the decomposition of benzoyl peroxide in benzene the yield of biphenyl increased from 50% to 90% when aromatic compounds with nitro group were added to the media, and they called the phenomenon "nitro group effect.[12]" However, in Fig. 1 the nitro group

TABLE 2. PHENYLATION OF NITRO COMPOUNDS WITH $PhN_2BF_4$ AND $NaNO_2$ IN DMSO

| Compound | Product | Yield (%) |
|---|---|---|
| *p*-Nitrotoluene | 3-Methyl-6-nitrobiphenyl | 38 |
| | 2-Methyl-5-nitrobiphenyl | 4 |
| *p*-Nitrochlorobenzene | 3-Chloro-6-nitrobiphenyl | 44 |
| | 2-Chloro-5-nitrobiphenyl | 6 |
| *m*-Dinitrobenzene | 2,6-Dinitrobiphenyl | 47 |
| | 2,4-Dinitrobiphenyl | 23 |
| 1,3,5-Trinitrobenzene | 2,4,6-Trinitrobiphenyl | 55 |



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[9] to be published

[10] C. Rüchardt and E. Merz, *Tetrahedron Lett.*, **1964**, 2431; C. Rüchardt and B. Freudenberg, *ibid.*, **1964**, 3623; C. Rüchardt, *Angew. Chem.*, **77**, 974 (1965).

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

[12] D. H. Hey, K. S. Y. Liang, M. J. Perkins and G. H. Williams, *J. Chem. Soc., C*, **1967**, 1153; G. B. Gill and G. H. Williams, *ibid., B*, **1966**, 880.

does not appear to be peculiar on the straight line representing a satisfactory Hammett relationship, and it seems that the high yield of nitrobiphenyl can be explained in terms of the conjugative effect alone.

This phenylation reaction appears to be a good method for the syntheses of substituted biphenyls. This method is more advantageous than Gomberg reaction in that even solid substrates can be phenylated in homogeneous media under very mild and non-alkaline conditions. The phenylations of several solid aromatic compounds were investigated, and the results are summarized in Table 2. Yields are fairly large and better than those of Ullmann reaction. It is interesting to note that the substitution with phenyl group takes place at the position ortho to sterically large nitro group in good yields. As an example, phenylations of *m*-dinitrobenzene by several methods[13] are compared above, and the comparison reveals the synthetic utility of the phenylation with $PhN_2BF_4$-$NaNO_2$ in DMSO.

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[13] P. E. Fanta, *Chem. Rev.*, **64**, 613 (1964); C. Björklund and M. Nilsson, *Tetrahedron Lett.*, **1966**, 675.