# Cationic Arylation. V.   Reaction of Substituted Benzenes with p-Nitrophenyl Cation

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The cationic arylation of substituted benzenes was investigated with p-nitrophenyl cation generated from p-nitrobenzenediazonium tetrafluoroborate in acetonitrile and from p-nitrophenylazo p'-tolyl sulfone in the presence of trifluoroacetic acid.   The isomer distribution of substituted nitrobiphenyls produced and the partial rate factors indicated electrophilic character of the p-nitrophenyl cation.   Selectivity of p-nitrophenyl cation is low compared with those of nitronium or sulfonyl cation, and similar to that of phenyl cation.   These facts suggest that the p-nitrophenyl cation functions as a cation diradical with concerted uncoupling of a pair of π-electrons, one of which falls into the vacant $sp^2$ σ-orbital.

Benzenediazonium tetrafluoroborate undergoes heterolysis in aprotic polar solvents, and substituted diphenyls are produced when some substituted benzene was present.   The partial rate factors in this phenylation are of electrophilic nature, and hence the reactive intermediate produced is considered to be phenyl cation.[1]   However, the positional selectivity of phenyl cation is considerably different from those of nitro, sulfonyl, alkyl, or acyl cations in ordinary electrophilic substitutions on arenes.[2]   Abramovitch et al.[3] modified a proposal originally made by Taft[4] concerning the stabilization of the m-methoxyphenyl cation, and suggested that aryl cation (I) initially formed in the thermal decomposition of diazonium salts may isomerize to a diradical cation (II) with concerted uncoupling of a pair of π-electrons, one of which falls into the vacant $sp^2$ σ-orbital, and that the resulting species would be expected to behave like a highly electrophilic free radical in aromatic substitution reactions.   Canonical structures (II) would have the properties of a triplet carbene.   If a second π-electron fell into the σ-orbital, the species (III) resulted might behave as a singlet carbene.
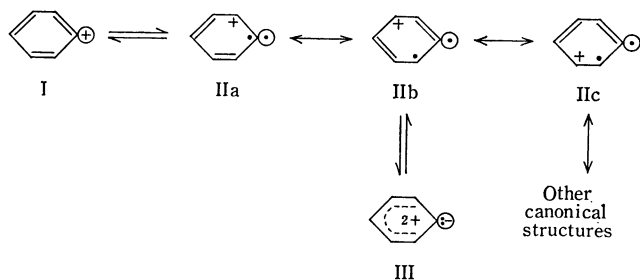


Preliminary molecular-orbital calculations made by Absar and McEwen[5] indicate the order of stabilization

(II)>(III)>(I) for the phenyl cation itself, the triplet diradical cation (II) being the ground state.

In an attempt to study further the electronic state of phenyl cation, the isomer distributions and partial rate factors in substitutions of arenes with p-nitrophenyl cation have been investigated.   The results will be described in this paper.

## Results and Discussion

p-Nitrophenyl cation was generated from p-nitrobenzenediazonium tetrafluoroborate in acetonitrile or from p-nitrophenylazo p'-tolyl sulfone and trifluoroacetic acid.   A substituted benzene was mixed with the p-nitrophenyl cation source, and the isomer distributions and partial rate factors in the p-nitrophenylation were determined.   Table 1 and 2 show the results, together with the data on phenyl cation[1b,6] and p-nitrophenyl radical[7] for comparison.

The data in Table 1 show that p-nitrophenyl cation, not p-nitrophenyl radical, is produced, since with nitrobenzene as the substrate the meta position of the nitrobenzene is substituted extensively and the partial rate factors are much smaller than unity and quite different from those with p-nitrophenyl radical.

Zollinger reported that when p-nitrobenzenediazonium tetrafluoroborate was decomposed in a mixture of nitrobenzene and DMSO, the isomer distribution of the 4,X'-dinitrodiphenyls produced was ortho 65.3, meta 9.5 and para 25.2%.[8]   Since this isomer distribution is similar to that with p-nitrophenyl radical produced from p-nitrobenzoyl peroxide, he proposed that p-nitrobenzenediazonium cation combines with DMSO, forming an intermediate, which then decomposes to p-nitrophenyl radical, nitrogen and DMSO cation radical.   Our results are quite different from Zollinger's, and the difference can be ascribed to the solvents; all the data are in agreement with the interpretation that in acetonitrile p-nitrobenzenediazonium ion forms p-nitrophenyl cation whereas it forms p-nitrophenyl radical in DMSO.

When the partial rate factors with phenyl cation and

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

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

8) H. Zollinger, The abstract of Post ISNA Symposium held in Tokyo, Aug. 30, 1970.

Table 1. Isomer distributions and partial rate factors in the arylation of aromatic substrates with $XC_6H_4N_2BF_4$ in acetonitrile at 60°C

| Substrate | Arylating reagent | Isomer distributions | | | $m/p$ | Partial rate factors | | |
|---|---|---|---|---|---|---|---|---|
| | | o- | m- | p- | | $f_o$ | $f_m$ | $f_p$ |
| $C_6H_5OCH_3$ | $C_6H_5N_2BF_4$ (I)[a] | 64.7 | 8.4 | 26.9 | 0.31 | 1.77 | 0.23 | 1.47 |
| | $p$-$NO_2C_6H_4N_2BF_4$ (II)[b] | 55.0 | 13.1 | 31.9 | 0.41 | 2.55 | 0.61 | 2.96 |
| | $p$-$NO_2C_6H_4N(NO)COCH_3$ (III)[c] | 72 | 12 | 16 | 0.75 | 5.17 | 0.84 | 2.30 |
| $C_6H_5Cl$ | (I)[a] | 59.8 | 15.2 | 25.0 | 0.61 | 0.67 | 0.17 | 0.56 |
| | (II)[b] | 55.6 | 23.4 | 21.0 | 1.11 | 1.01 | 0.43 | 0.77 |
| | (III)[c] | 57 | 24 | 19 | 1.26 | 1.53 | 0.65 | 1.01 |
| $C_6H_5NO_2$ | (I)[a] | 32.3 | 48.4 | 19.3 | 2.53 | 0.10 | 0.15 | 0.12 |
| | (II)[b] | 50.0 | 46.9 | 3.1 | 15.1 | 0.16 | 0.15 | 0.02 |
| | (III)[c] | 46 | 17 | 37 | 0.46 | 0.93 | 0.35 | 1.53 |

a) Ref. 1b    b) This work    c) Ref. 7

Table 2. Isomer distributions and partial rate factors in the arylation of aromatic substrates with $XC_6H_4N_2Ts$ in the presence of $CF_3CO_2H$ at 60°C

| Substrate | Arylating reagent | Isomer distributions | | | $m/p$ | Partial rate factors | | |
|---|---|---|---|---|---|---|---|---|
| | | o- | m- | p- | | $f_o$ | $f_m$ | $f_p$ |
| $C_6H_5OCH_3$ | $C_6H_5N_2Ts$ (I)[a] | 76.0 | 4.8 | 19.2 | 0.25 | 2.66 | 0.17 | 1.34 |
| | $p$-$NO_2C_6H_4Ts$ (II)[b] | 77.7 | 9.9 | 12.4 | 0.88 | 3.97 | 0.51 | 1.27 |
| | $p$-$NO_2C_6H_4N(NO)COCH_3$ (III)[c] | 72 | 12 | 16 | 0.75 | 5.17 | 0.84 | 2.30 |
| $C_6H_5Cl$ | (I)[a] | 70.3 | 9.4 | 20.3 | 0.46 | 0.56 | 0.08 | 0.33 |
| | (II)[b] | 63.6 | 23.3 | 13.1 | 1.78 | 1.46 | 0.53 | 0.60 |
| | (III)[c] | 57 | 24 | 19 | 1.26 | 1.53 | 0.65 | 1.01 |
| $C_6H_5NO_2$ | (I)[a] | 27.2 | 67.8 | 5.0 | 13.6 | 0.08 | 0.19 | 0.03 |
| | (II)[b] | 82.8 | 11.0 | 6.2 | 1.77 | 0.88 | 0.12 | 0.13 |
| | (III)[c] | 46 | 17 | 37 | 0.46 | 0.93 | 0.35 | 1.53 |

a) Ref. 6    b) This work    c) Ref. 7

those with $p$-nitrophenyl cation are compared, the latter are greater with all the substrates (except $f_p$ with nitrobenzene). $p$-Nitrophenyl cation is more selective than phenyl cation, and according to Brown's selectivity rule $p$-nitrophenyl cation is considered to be less reactive than phenyl cation.

When the $m/p$ ratios are compared in order to examine the selectivity within a molecule, they are always greater with $p$-nitrophenyl cation than with phenyl cation. This finding also shows that $p$-nitrophenyl cation is less reactive than phenyl cation. This intramolecular selectivity is greater with the substrate with an electron-withdrawing substituent and hence less prone to make a bond with an aryl cation. This is reasonable since the activation energy is greater with less reactive substrates, the transition state is at a later stage on the reaction coordinate and hence the intramolecular selectivity is greater.
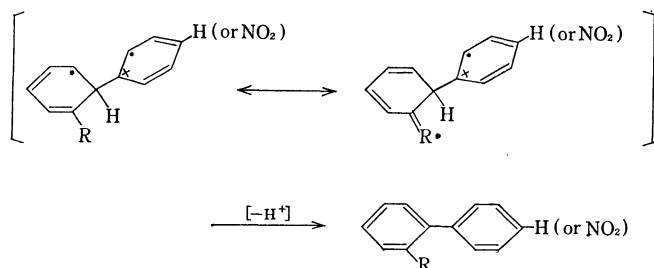


The yields of ortho isomers are always great, and this shows the radical nature of aryl cations. An intermediate σ-complex can be expressed as shown in the above structural formula and it roughly approximates the transition state. The more stable structure is that possessing the substituent R at the end of the resonance system of the cyclohexadienyl radical, and it gives rise to the ortho isomer.

The data shown in Table 2 also indicate that both the intermolecular (the partial rate factors) and intramolecular (the $m/p$ ratios) selectivities of $p$-nitrophenyl cation are in general greater than those of phenyl cation. Hence, $p$-nitrophenyl cation is less reactive than phenyl cation.

The comparison of the data in Table 1 and 2 reveals that the isomer distributions and partial rate factors somewhat differ when the source and the medium are different. Such differences could be ascribed to the following reasons. 1) Difference of the counter anions: The counter anion is $BF_4^-$ in the case of the diazonium salts and $CF_3CO_2^-$ (or $ArSO_2^-$) in the case of the azosulfones. The tightness of the ion pairs naturally differs. 2) Difference in the rates of abstraction of proton from the σ-complex: Since the basicities of the counter anions differ, the rates of proton abstraction may be different. However, no isotope effect was observed as reported in a previous paper,[1b] and hence the rate-determining step must be the forma-

tion of the σ-complex.   3) Difference in the solvents: The diazonium salts are decomposed in acetonitrile which is fairly basic, and therefore fairly extensive solvation is expected at the transition state although smaller than that at the ground state. The medium in which azosulfones are decomposed contains about 20% trifluoroacetic acid, and the solvation is expected to be very little. The fact that $f_m$ and $f_p$ are smaller with azosulfones could be ascribed to lack of stabilization by solvation at the transition state.

The reactivities at the *ortho* positions are somewhat greater in azosulfones than those in diazonium salts, and especially the values with *p*-nitrophenyl cation toward the *ortho* position of nitrobenzene are unusually great. At present, it is not possible to give an adequate explanation to this finding.

The fact that *p*-nitrophenyl cation is more selective and less reactive than phenyl cation in reactions with arenes could be explained as follows.   If phenyl cation and *p*-nitrophenyl cation do not possess diradical cation nature, certainly *p*-nitrophenyl cation would be less stable and more reactive than phenyl cation. However, *p*-nitrophenyl cation is stabilized considerably by resonance with the nitro group as shown below. Thus, because of the diradical cation nature of the aryl cations, *p*-nitrophenyl cation is more stable and less reactive than phenyl cation.
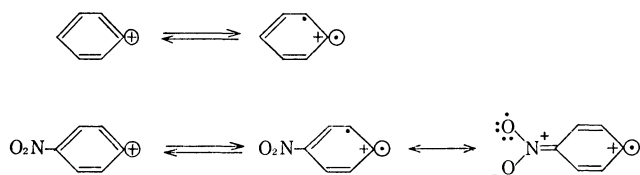


## Experimental

*Materials.*        Acetonitrile was purified according to the method in the literature[9] and distilled; bp 81.5°C. Trifluoroacetic acid of Wako Pure Chemical Industries Limited was used without further purification. Benzene and chlorobenzene were washed with concentrated sulfuric acid and water successively, dried over calcium chloride and distilled. Boiling points were 80 and 131°C, respectively. Anisole was washed with an aqueous sodium hydroxide solution and water, dried over calcium chloride, and distilled; bp 153°C. Nitrobenzene was washed repeatedly with a potassium dichromate solution, dried over calcium chloride, and distilled; bp 95.5°C/18 mmHg.

*p*-Nitrobenzenediazonium tetrafluoroborate was prepared according to the method described in the literature.[10]

*p*-Nitrophenylazo *p*'-tolyl sulfone was prepared according to the method described previously.[11]

4-Nitrodiphenyl was prepared by nitration of diphenyl

according to the method of Maki and Obayashi,[12] mp 112.8—113°C (from methanol).

2-Methoxy-4'-nitrodiphenyl was prepared from *N*-nitroso-*p*-nitroacetanilide[13] and anisole, and was purified by elution chromatography and recrystallized from methanol, mp 63—64°C.

3-Methoxy-4'-nitrodiphenyl was prepared from diazotized *m*-anisidine and nitrobenzene by the Gomberg reaction. After removal of the solvent from the reaction mixture, the residue was distilled with superheated steam. The crystals obtained were then fractionated by chromatography on alumina in *n*-hexane–benzene (1: 1), mp 90—91°C (from methanol).

4-Methoxy-4'-nitrodiphenyl was prepared from *N*-nitroso-*p*-acetanisidide[12] and nitrobenzene, and was purified by elution chromatography on alumina in *n*-hexane–benzene and recrystallized from methanol, mp 110°C.

2-Chloro-4'-nitrodiphenyl was prepared by reaction of *N*-nitroso-*p*-nitroacetanilide[13] with chlorobenzene. After removal of chlorobenzene under reduced pressure, distillation with superheated steam and then elution chromatography on alumina (*n*-hexane–benzene, 4:1), yielded the product, mp 79—80°C (from methanol).

3-Chlorodiphenyl and 4-chlorodiphenyl were prepared by the method reported previously.[14]

3-Chloro-4'-nitrodiphenyl was prepared by the nitration of 3-chlorodiphenyl with fuming nitric acid in acetic anhydride. The crude oily product was fractionally distilled under reduced pressure (bp 157—160°C/1 mmHg) and purified by elution chromatography on alumina in *n*-hexane–benzene (4: 1); mp 93—94°C (from methanol).

4-Chloro-4'-nitrodiphenyl was prepared by the nitration[15] of 4-chlorodiphenyl, and was then purified by elution chromatography on alumina in *n*-hexane–benzene and recrystallized from ethanol; mp 145.5°C.

2,4'- and 4,4'-Dinitrodiphenyl were prepared by the nitration of 4-nitrodiphenyl according to the method of Maki and Obayashi.[12] The 2,4'-isomer was recrystallized from ethanol (mp 93.5—94°C), and the 4,4'-isomer from acetone (mp 237°C).

3-Nitrodiphenyl was prepared by the method described in the literature.[16]

3,4'-Dinitrodiphenyl was prepared by the nitration of 3-nitrodiphenyl according to the method reported in the literature,[17] mp 188.5°C (from ethanol).

*General Procedure for* p-*Nitrophenylation with* p-*Nitrobenzenediazonium Tetrafluoroborate.*        In acetonitrile (70.0 g) *p*-nitrobenzenediazonium tetrafluoroborate (2.1 g) was dissolved, and the solution was diluted with an equimolar mixture of benzene and monosubstituted benzene (50 mol of the total substrate/mol of *p*-NO$_2$C$_6$H$_4$N$_2$BF$_4$). The homogeneous solution was placed in a bath at 60±0.1°C, and the decomposition was followed by measuring the evolution of nitrogen. After the evolution of nitrogen ceased, the mixture was diluted with ether and triphenylmethane was added as an internal standard for the glc analyses. The ethereal solution was washed with water to remove the acetonitrile,

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15) C. K. Bradsher and L. J. Wissow, *J. Amer. Chem. Soc.*, **68**, 404 (1946).

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17) R. Ito, T. Migita, N. Morikawa, M. Okuni, and O. Simamura, This Bulletin, **36**, 985 (1963).

washed with a 5% sodium hydroxide solution to remove acidic products, and water successively, and dried over anhydrous magnesium sulfate.

*General Procedure for* p-*Nitrophenylation with* p-*Nitrophenylazo* p'-*Tolyl Sulfone in the Presence of Trifluoroacetic Acid.*
p-Nitrophenylazo p'-tolyl sulfone (2.0 g, 6.6 mmol) was dissolved in a mixture of benzene (0.250 mol) and a substituted benzene (0.250 mol), and then trifluoroacetic acid (6.0 g, 52.6 mmol) was added to this homogeneous solution. The mixture was decomposed in a constant temperature bath at 60±0.1°C. After the decomposition was over, the reaction mixture was treated in a manner similar to that described for the reaction with p-nitrobenzenediazonium tetrafluoroborate.

*Quantitative Analyses.* The substituted nitrodiphenyl isomers produced in the p-nitrophenylation were separated by gas chromatography. The compounds corresponding to the individual peaks were identified by comparing their retention times with those of the authentic specimens and their amounts were determined by use of calibration curves. The columns used were packed with Apiezon L (10%) on Chromosorb W, 1 m.