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Cationic Arylation. III. Comparison of Phenylation of Naphthalene with Phenyl Cation and Phenyl Radical

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Naphthalene was phenylated with phenyl cation (from PhN_2BF_4) or phenyl radical (from $PhN_2BF_4+NaNO_2$) in dimethyl sulfoxide. Partial rate factors for phenyl radical were somewhat larger than those reported with the phenyl radical generated from *N*-nitrosoacetanilide. Partial rate factors for phenylation with phenyl cation were smaller than those for free radical phenylation and those for common electrophilic substitution reactions. These small partial rate factors for phenyl cation were not compatible with the reaction scheme involving an ordinary σ-complex, and a mechanism involving a spiro cation appeared to be plausible.

In previous papers,[1,2] we reported that phenyl cation was formed from benzenediazonium tetrafluoroborate or phenylazo-*p*-tolylsulfone. The orientation and the partial rate factors for this phenylation appeared to support the hypothesis that the phenyl cation [I] initially formed isomerized to a diradical cation [II] with concerted uncoupling of a pair of π-electrons. However, the mechanism

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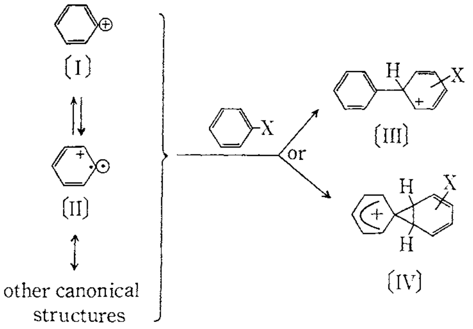
[1] M. Kobayashi, H. Minato, E. Yamada and N. Kobori, This Bulletin, **43**, 215 (1970).

[2] M. Kobayashi, H. Minato and N. Kobori, *ibid.*, **43**, 219 (1970).

of the substitution was not completely clear, especially as to whether or not a spiro cation [IV] was the intermediate.



In order to clarify the nature of the phenyl cation and the mechanism of the phenylation, the electrophilic substitution with phenyl cation has been investigated with naphthalene as the substrate, and the results are described in this paper.

Since the isomerization of phenyl cation to a diradical has been postulated, it is of great interest to compare phenylation by phenyl cation with that by phenyl radical. Therefore, the phenylation of naphthalene by the phenyl radical produced from benzenediazonium tetrafluoroborate and sodium nitrate[3] has been investigated, and the results will be compared with those obtained with phenyl cation.

Experimental

Materials. Preparation of benzenediazonium tetrafluoroborate and purification of dimethyl sulfoxide (DMSO) and anisole were previously reported.[1] Naphthalene, extra pure grade of Kanto Chemicals, was used without further purification. α-Phenylnaphthalene, bp 167°C/8 mmHg (lit,[4] 180°C/10 mmHg) and *β*-phenylnaphthalene, mp 102°C (lit,[4] 103—104°C) were prepared according to the methods described in literature.[4]

Phenylation of Naphthalene with Benzenediazonium Tetrafluoroborate in DMSO. In 20 g of DMSO 2.0 g of benzenediazonium tetrafluoroborate was dissolved and the solution was added to an anisole-naphthalene mixture (the molar ratio of aromatic compounds *versus* the diazonium salts was 50). The homogeneous solution obtained was decomposed in a bath at 40 ± 0.1°C. After the evolution of nitrogen gas ceased, ether was added to the reaction mixture. This mixture was washed with water to remove DMSO, with a 5% sodium hydroxide solution to remove acidic products and then with water. After it was dried over magnesium sulfate, ether, anisole and naphthalene in this mixture were removed in a vacuum. After about 70% of anisole and naphthalene was removed, the residual oil containing arylated products was analyzed by a Hitachi Gas Chromatograph K-53.

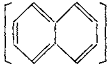
Phenylation of Naphthalene with Benzenediazonium Tetrafluoroborate and Sodium Nitrite in DMSO. Anisole (37.056 g, 0.3427 mol), naphthalene (9.748 g, 0.0761 mol) and sodium nitrite (1.736 g, 0.0253 mol) were dissolved in 100 g of DMSO, and this homogeneous solution was stirred vigorously with a mechanical stirrer. Under a nitrogen atmosphere, a solution of 1.467 g of benzenediazonium tetrafluoroborate in 10 g of DMSO was added dropwise into the above solution. Nitrogen gas was evolved immediately and the reaction was complete as soon as the diazonium salt solution was added. The reaction mixture was treated in a manner similar to that described above for the case in the absence of sodium nitrite.

Quantitative Analyses. Methoxybiphenyl isomers and phenylnaphthalene isomers were identified by comparison of their retention times with those of authentic samples, and their amounts were determined by use of calibration curves on a 2 m column packed with Apiezon L (10%) on Chromosorb W at 200°C with a gas-flow of 30 m*l*/min.

Results and Discussion

Anisole, instead of benzene, was used for competitive phenylation, since non-substituted biphenyls is lost by sublimation during the concentration of the reaction mixture prior to gas-chromatographic analyses. The attack of both phenyl cation and phenyl radical on the aromatic hydrocarbons

Table 1. Orientation and partial rate factors for phenylation of naphthalene

Run	[$PhOCH_3$]/[]	Orientation (%)		Partial rate factors	
		α-	*β*-	α-	*β*-
1[a]	0.979	73.0	27.0	3.36	1.24
2[a]	2.964	76.6	23.4	2.95	0.90
3[a]	5.774	78.7	21.3	2.92	0.74
4[b]	4.38	80.6	19.4	16.48	3.98
5[b]	4.50	77.5	22.5	13.13	3.81
6[c]				11.29	1.10
7[c]				13.71	1.34
8[d]				470	50
9[e]				2.1×10^5	2.1×10^3
10[f]				178	23.4

a) Phenylation with PhN_2BF_4 in DMSO at 40°C (Phenylation with phenyl cation)
b) Phenylation with PhN_2BF_4 and $NaNO_2$ in DMSO (Phenylation with phenyl radical)
c) Phenylation with *N*-nitrosoacetanilide, D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, **1961**, 3112.
d) Nitration, R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publ. Co., Amsterdam, London, New York (1965), p. 88.
e) Bromination in aq. AcOH, *ibid.*, p. 150
f) Deuteration, *ibid.*, p. 220

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[3] M. Kobayashi, H. Minato, E. Yamada and N. Kobori, This Bulletin, to be published

[4] R. Adams, Ed. "Organic Reactions," Vol. II, p. 258 (1960).

resulted in the formation of methoxybiphenyl isomers and phenylnaphthalene isomers, but the compositions of these phenylated products were quite different from each other.

As products other than methoxybiphenyls and phenylnaphthalenes, 1,3-benzoxathian was obtained from the decomposition of benzenediazonium tetrafluoroborate in the absence of sodium nitrite, but not in the presence of sodium nitrite.

The orientation and partial rate factors for phenylation with phenyl cation and with phenyl radical are compared with other related data in Table 1. The orientation and the partial rate factors for phenylation with phenyl cation change to some extent with the molar ratio of naphthalene *versus* anisole.

The partial rate factors for phenylation with the phenyl radical generated from benzenediazonium tetrafluoroborate and sodium nitrite are a little larger than those obtained by Davies, Hey and Williams with the phenyl radical generated from *N*-nitrosoacetanilide as shown in Table 1. It is not easy to determine what is responsible for this difference in the partial rate factors. One could ascribe it to the effect of the polar solvent (DMSO) present in our medium, or to the difference in the hydrogen-abstracting species. However, we recently found that the partial rate factors for the phenylation with the phenyl free radical generated from phenylazotriphenylmethane were not influenced to any appreciable extent by the presence of the polar solvent DMSO.[5] Therefore, it does not seem to be possible to attribute this difference to the effect of solvents.

As for the hydrogen abstracting species, both NO_2 and PhN=NO· are conceivable as the hydrogen-abstracting species in a reaction mixture of benzenediazonium tetrafluoroborate and sodium nitrite as shown in Schemes 1 and 2.

$$PhN_2BF_4 + NaNO_2 \longrightarrow PhN{=}N{-}O{-}NO + NaBF_4$$

Scheme 1

$$PhN{=}N{-}O{-}NO \longrightarrow Ph\cdot + N_2 + NO_2$$

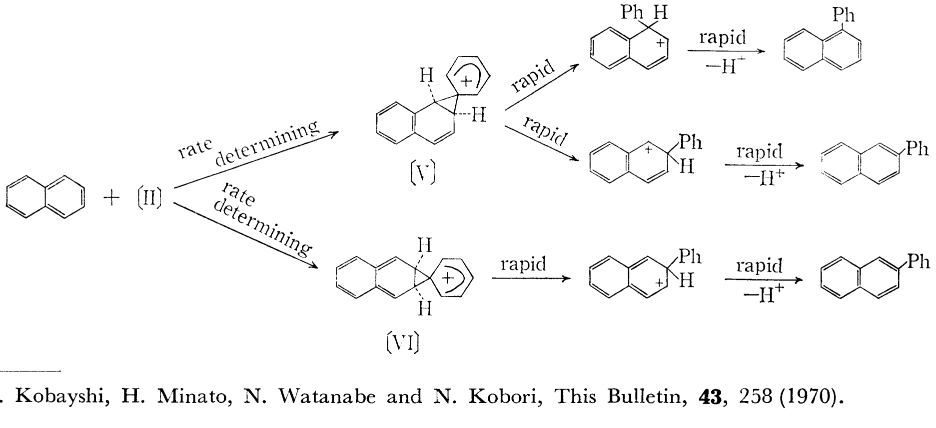
Scheme 2

$$2\,PhN{=}N{-}O{-}NO \longrightarrow PhN{=}N{-}O{-}N{=}N{-}Ph + N_2O_3$$

$$PhN{=}N{-}O{-}N{=}N{-}Ph \longrightarrow Ph\cdot + N_2 + PhN{=}N{-}O\cdot$$

In order to clarify the difference in the partial rate factors due to the origin of the phenyl radicals, the hydrogen-abstracting species in the mixture of benzenediazonium tetrafluoroborate and sodium nitrite must be identified. Such an investigation is being carried out.

As shown in Table 1, the partial rate factors for phenylation with phenyl cation are much smaller than those for nitration, bromination and deuteration, which are typical electrophilic substitution reactions. These data appear to support the hypothesis that the phenyl cation is not an ordinary cation [I] but a diradical cation [II]. If the phenyl cation is an electrophilic radical possessing the properties of both a cation and a radical, it is expected that the values of the partial rate factors for the phenylation with the phenyl cation come between those with electrophilic reagents and those with phenyl radical. However, on the contrary to such expectation, the partial rate factors with phenyl cation were smaller than both of these. A mechanism with which one could explain these findings is the following one, involving the spiro cations [V] and [VI] as the intermediates.



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