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Cationic Arylation. VI. Phenylation of Arenes with Benzenediazonium Trifluoroacetate

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Nesmeyanov *et al.* first reported that the decomposition of aryldiazonium tetrafluoroborate in aromatic solvents yields aryl cation as a reactive intermediate which attacks the aromatic nucleus, forming biaryls.[1] However, concerning the substitution of arenes with aryl cation only few papers have been published, mainly by Abramovitch *et al.*[2]

The investigations carried out in our laboratories on cationic arylation have established that phenyl cation can readily be generated by one of the following three routes; a) thermal decomposition of benzenediazonium tetrafluoroborate in aprotic polar solvents,[3] b) thermal decomposition of phenylazo *p*-tolyl sulfone in the presence of trifluoroacetic acid,[4] and c) thermal decomposition of phenylazotriphenylmethane in tri-

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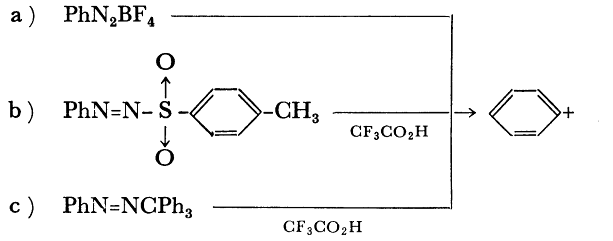
[1] A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolustaya, *Tetrahedron*, **1**, 145 (1957).

[2] R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **23**, 3269 (1965); R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc., B*, **1968**, 497.

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

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

fluoroacetic acid.[5]



Benzenediazonium trifluoroacetate (I) was first prepared and isolated by Pettit *et al.*[6] They concluded that phenyl radical was an intermediate simply because biphenyl was found in 24% yield when I was decomposed in benzene. This conclusion contradicts with our hypothesis that in the decomposition of phenylazo *p*-tolyl sulfone[4] or phenylazotriphenylmethane[5] in trifluoroacetic acid I is formed in the first step and subsequently degrades, not to phenyl radical, but to phenyl cation. Since I may exist either in the covalent diazoacetate structure ($Ph-N=N-O_2CCF_3$) which will give aryl free radical or in the ionic diazonium ion pair form ($PhN_2^+CF_3CO_2^-$) which should yield aryl cation, its decomposition mechanism can be formulated in terms of these two reactive species.

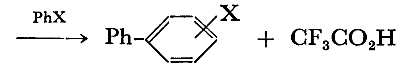
In order to clarify the mechanism of the decomposition of I, phenylation of arenes by I has been investigated, and the isomer distributions and partial rate factors in the phenylation have been determined. The results are described in this paper.

Results and Discussion

Phenylation of Arenes. I is insoluble in aromatic solvents and soluble in water and such aprotic polar solvents as acetonitrile and nitromethane. Therefore, I was decomposed in arene–acetonitrile mixture in order to carry out the phenylation in homogeneous solution. The isomer distributions and partial rate factors determined are compared in Tables 1 and 2 with the data reported in the literature. The isomer distributions of phenylarenes are quite similar to those obtained in the phenylation with benzenediazonium tetrafluoroborate,[3] phenylazo *p*-tolyl sulfone in the presence of trifluoroacetic acid,[4] and phenylazotriphenylmethane in trifluoroacetic acid,[5] but significantly differ from the values observed in the phenylation with *N*-nitrosoacetanilide.[7] Namely, in the former cases the methoxy, ethyl and chloro groups behaved as *o,p*-directors and nitro group behaved as a *m*-director, whereas in the latter case the nitro group behaved as an *o,p*-director.

The partial rate factors observed with I are also similar to the values in the phenylation with benzenediazonium tetrafluoroborate,[3] phenylazo *p*-tolyl sulfone[4] or phenylazotriphenylmethane[5] in trifluoroacetic acid but different from the figures reported for phenylation with *N*-nitrosoacetanilide.[7] These results clearly show that the decomposition of I does not yield phenyl radical, but yields phenyl cation. Thus, I is a new reagent for production of phenyl cation, and one can choose from PhN_2BF_4, $PhN_2O_2SAr+CF_3CO_2H$, $PhN_2CPh_3+CF_3CO_2H$, and $PhN_2O_2CCF_3$ (I).

$$PhN_2^+CF_3CO_2^- \longrightarrow Ph^+ + N_2 + CF_3CO_2^-$$



Reaction with Oxygen^{18}*-enriched Water.* When I was dissolved in water and decomposed at 25°C, phenol was obtained in 60—65% yield. This finding further supports the ionic decomposition mechanism and the formation of phenyl cation as a reactive intermediate. The reaction seems to be a convenient method for preparation of phenols, especially for preparation of ^{18}O-labeled phenols. When I was decomposed in water containing 1.3 atom % excess ^{18}O, phenol with 0.89 atom % excess ^{18}O was obtained in

TABLE 1. ISOMER DISTRIBUTIONS OF PHENYLARENES PRODUCED BY PHENYLATION OF ARENES WITH VARIOUS PHENYLATING AGENTS

X	Position	PhC_6H_4X produced (%) by				
		$PhN_2^+CF_3CO_2^-$	$PhN_2^+BF_4^-$[3]	PhN_2Ts in CF_3CO_2H[4]	PhN_2CPh_3 in CF_3CO_2H[5]	PhN(NO)Ac[7]
$-OCH_3$	*o*	61.6	51.0	45.6	43.9	69
	m	9.7	6.6	8.2	8.1	18
	p	28.7	42.4	46.2	48.0	13
$-C_2H_5$	*o*	45.5	39.6	41.1	20.7	71[a]
	m	28.1	21.0	20.7	10.6	18[a]
	p	26.4	39.4	38.2	68.7	11[a]
-Cl	*o*	55.2	47.9	39.2	58.1	64
	m	19.9	12.1	14.4	10.5	21
	p	24.9	40.0	46.4	31.4	15
$-NO_2$	*o*	27.8	27.0	17.6	21.3	62
	m	69.4	40.6	37.3	72.3	8
	p	2.8	32.4	45.1	6.4	30

a) Isomer distribution of $PhC_6H_4CH_3$.

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[5] N. Kamigata, M. Kobayashi, and H. Minato, *ibid.*, **45**, 1231 (1972).

[6] M. R. Pettit, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, **1953**, 3081; M. R. Pettit and J. C. Tatlow, *ibid.*, **1954**, 1941.

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

TABLE 2. PARTIAL RATE FACTORS IN THE PHENYLATION OF C_6H_5X WITH VARIOUS PHENYLATING AGENTS

Arenes	Position	Partial rate factor in the reaction with				
		$PhN_2{}^+CF_3CO_2{}^-$	$PhN_2{}^+BF_4{}^-$[3]	PhN_2Ts in CF_3CO_2H[4]	PhN_2CPh_3 in CF_3CO_2H[5]	PhN(NO)Ac[7]
$C_6H_5OCH_3$	*o*	2.66	1.77	1.72	1.52	3.56
	m	0.42	0.23	0.31	0.28	0.93
	p	2.48	1.47	1.74	1.66	1.29
$C_6H_5C_2H_5$	*o*	1.46	1.45	1.57	1.80	3.7[a]
	m	0.90	0.77	0.79	0.92	0.9[a]
	p	1.69	1.44	1.46	5.99	1.1[a]
C_6H_5Cl	*o*	0.83	0.67	0.60	0.89	3.09
	m	0.30	0.17	0.22	0.16	1.01
	p	0.75	0.56	0.71	0.48	1.48
$C_6H_5NO_2$	*o*	0.10	0.10	0.09	0.10	9.38
	m	0.25	0.15	0.19	0.34	1.16
	p	0.02	0.12	0.23	0.03	9.15

a) Partial rate factor with toluene.

61% yield.

Oxygen-18 labeled phenols could be produced by such methods as 1) $ArMgX+{}^*O_2$, 2) $ArSO_3Na+Na^*OH$, 3) $ArX+Na^*OH$ and 4) $ArN_2BF_4+CH_3C^*O_2H \rightarrow Ar^*OAc \rightarrow Ar^*OH$. The method 1) requires ^{18}O-enriched oxygen gas which is not commercially available. The method 2) and 3) require Na^*OH and rather high temperatures. The method 4) requires large excess of $CH_3C^*O_2H$ which is also not commercially available. Hydrolysis of $PhN_2{}^+BF_4{}^-$ or $PhN_2{}^+Cl^-$ in $H_2{}^*O$ needs high temperature and tends to give phenol with a lot of tarry mixture. On the contrary, the reaction between I and $H_2{}^{18}O$ proceeds smoothly at room temperature, the procedure is very simple, and therefore, one can say that this method is most convenient for preparation of ^{18}O-labeled phenol.

Experimental

Materials. I was prepared by diazotization of aniline with a concentrated aqueous solution (*ca.* 40%) of sodium nitrite in trifluoroacetic acid at 0—5°C. The crystals formed were filtered off, washed with small quantities of ice-water, and then dried for several hours *in vacuo* at 0°C over phosphorus pentoxide.[6] Purification of benzene and several arenes and preparation of authentic samples of substituted biphenyls were described previously.[3]

General Procedure for Determination of the Relative Reactivities of PhX toward Benzenediazonium Trifluoroacetate in Acetonitrile. A solution of I (2.0 g) in acetonitrile (2.0 g) was diluted with an equimolar mixture of PhH and PhX (the molar ratio (PhH+PhX)/I was 75). The homogeneous solution was placed in a bath at 20±0.1°C, and the decomposition was followed by evolution of nitrogen. After the evolution of nitrogen ceased, the reaction mixture was washed with water, a 5% sodium hydroxide solution, water, and then dried over anhydrous magnesium sulfate. The amounts of substituted biphenyl isomers were determined by a Hitachi Gas Chromatograph K-53 (Apiezon L 10% on Chromosorb W).

Not benzene but chlorobenzene was used as the standard for the competitive phenylation of PhOMe, PhEt, and $PhNO_2$, since unsubstituted biphenyl easily sublimes during the evaporation of arenes.[3-5]

Preparation of ^{18}O-labeled Phenol. Dry I (53 g) was dissolved in 70 ml of water (1.3 excess atom % ^{18}O) and spontaneously decomposed at 25°C. After the evolution of nitrogen ceased, the reaction mixture was diluted with ether, washed with water and dried over anhydrous magnesium sulfate. Oxygen-18 excess phenol was isolated by distillation under reduced pressure, bp 70°C/30 mmHg, yield 6.2 g (61%).

Determination of Oxygen-18 Contents. Phenol was brominated to 1,3,5-tribromophenol, which was purified by sublimation three times, and then converted into carbon dioxide according to the method of Rittenberg and Ponticorvo[8] for determination of the oxygen-18 contents. The ^{18}O-contents of the carbon dioxide was determined by use of a Hitachi RM-50 Type Mass Spectrometer.

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8) D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Radiat. Isotopes*, **1**, 208 (1956).