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Cationic Arylation. II. Phenylation of Substituted Benzenes with Phenylazo-*p*-tolylsulfone in Acidic Solutions

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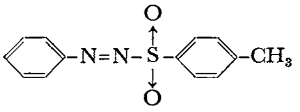
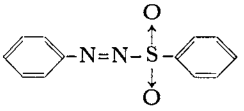
The acid-catalyzed decomposition of phenylazo-*p*-tolylsulfone was studied in PhX, PhX-CH_3CN and PhX-DMSO (X=OCH_3, C_2H_5, CH_3, Cl, CO_2CH_3, NO_2). The decomposition was of first order but was faster with greater concentration of trifluoroacetic acid. The orientation and the partial rate factors for the phenylation of substituted benzenes were quite different from those for the radical phenylation but quite similar to those for the phenylation with phenyl cation generated from $PhN_2^+BF_4^-$. Experiments with deuterated compounds indicated that the abstraction of proton from the phenylated complex was not rate-determining. A mechanism involving phenyl cation was proposed for the acid-catalyzed decomposition of azosulfone.

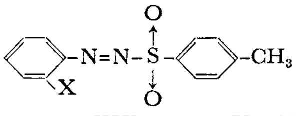
Phenylazo-*p*-tolylsulfone [I] is produced when an aqueous benzenediazonium chloride solution is mixed with an aqueous sodium *p*-toluenesulfinate solution. It is not an ionic compound, and is soluble in organic solvents and insoluble in water. When heated in a solution, it decomposes with evolution of nitrogen.



[I]



[II]



[III] X=Cl, Br

Overberger and Rosenthal[1] studied the kinetics of the decomposition of phenylazophenylsulfone [II] in neutral solutions, and found that its spontaneous decomposition was a free radical decomposition. Bunnett and Happer[2] investigated the decomposition of *o*-halophenylazophenylsulfone [III] in the presence of sodium methoxide, and found that in very dilute sodium methoxide solution the decomposition was homolytic, whereas in concentrated sodium methoxide solution the decomposition proceeded *via* *o*-halophenyl anion as the intermediate.

It seemed of great interest to investigate the decomposition of azosulfones in acidic solutions. The decomposition of phenylazo-*p*-tolylsulfone [I] in the presence of trifluoroacetic acid in substituted benzenes has been investigated, and the results are described in this paper.

Experimental

Materials. Dimethyl sulfoxide, acetonitrile and substituted benzenes were purified according to the methods described in a previous paper.[3]

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[1] C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, **82**, 108, 117 (1960).

[2] J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **32**, 2701 (1967).

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

Sodium *p*-toluenesulfinate was prepared by the reduction of *p*-toluenesulfonyl chloride with zinc.[4]

Phenylazo-*p*-tolylsulfone was prepared by mixing an aqueous benzenediazonium chloride solution with an aqueous sodium *p*-toluenesulfinate solution at 5°C,[5] and was recrystallized from methanol. Mp 91—92°C.

Kinetic Measurements. To a solution consisting of 2.6 g (0.01 mol) of phenylazo-*p*-tolylsulfone and 39 g (0.5 mol) of benzene, some trifluoroacetic acid was added, and the solution was placed in a constant temperature bath. The rate of nitrogen evolution was measured by a gas burette.

Analyses of Phenylation Products. Phenylazo-*p*-tolylsulfone (2.6 g) was dissolved in a substituted benzene, and trifluoroacetic acid was added; the mixture consisted of 50 mol of a substituted benzene and 5.89 mol of trifluoroacetic acid per mole of phenylazo-*p*-tolylsulfone. The mixture was decomposed in a constant temperature bath at 40.0±0.1°C. In order to examine the effect of polar solvents, 20 g of dimethyl sulfoxide or acetonitrile was added to the above mixture, and these mixtures containing polar solvents were decomposed in a similar manner.

After the decomposition was over, the reaction mixture was washed successively with water, a 5% sodium hydroxide solution and water, and was then dried over anhydrous magnesium sulfate.

The amounts of substituted biphenyls produced were determined by a Hitachi Gas Chromatograph K-53 on a column packed with 10% Apiezon L on Chromosorb W, on the basis of the comparison with authentic samples.

Results and Discussion

Figure 1 shows that the rate of decomposition of phenylazo-*p*-tolylsulfone is of first order. However, the rate is dependent on the amount of trifluoroacetic acid added. Table 1 lists the first order rate constants in benzene at various temperatures in the presence of 5.89 mol or 2.95 mol of trifluoroacetic acid per mole of the azosulfone. These values are much greater than the rate constant obtained by Overberger and Rosenthal[1] for the homolytic decomposition of phenylazophenylsulfone in benzene with calcium oxide suspended ($k_1=2.2\times10^{-5}$ sec^{-1} at 70°C). This great difference cannot be ascribed to the effect of *p*-methyl substituent in phenylazo-*p*-tolylsulfone. These findings suggest that the mechanism of the decomposition in acidic solutions is different from that in neutral solutions.

TABLE 1. FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF *p*-TsN_2Ph IN BENZENE-CF_3CO_2H

(p-TsN_2Ph/CF_3CO_2H =5.89 mol/mol)		(p-TsN_2Ph/CF_3CO_2H =2.95 mol/mol)	
Temp. (°C)	$10^4 k_1$ (sec^{-1})	Temp. (°C)	$10^4 k_1$ (sec^{-1})
40.5	5.39	45.6	6.24
34.9	2.34	40.7	2.94
30.0	1.11	35.5	1.19
25.5	0.53		
E_a=28.7 kcal/mol		E_a=32.3 kcal/mol	
$\Delta S^{\ddagger}$=16.0 e.u./mol (25°C)		$\Delta S^{\ddagger}$=26.1 e.u./mol (25°C)	

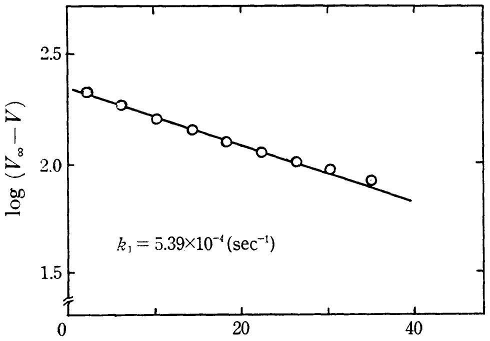

Fig. 1. First order rate plots for the decomposition of *p*-TsN_2Ph in benzene-CF_3CO_2H at 40.5°C. (*p*-TsN_2Ph/CF_3CO_2H=5.89 mol/mol)

Figure 2 is the Arrhenius plots of the rate constants shown in Table 1, and the values of the activation energies and the activation entropies were calculated from Fig. 2. These activation parameters fit surprisingly well the isokinetic relationship established for the decomposition of benzenediazonium tetrafluoroborate in various aprotic polar solvents,[6] as shown in Fig. 3. On the basis of these

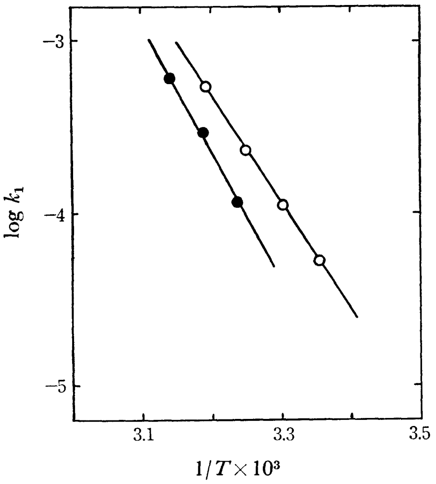

Fig. 2. The Arrhenius plots for the decomposition of *p*-TsN_2Ph in benzene-CF_3CO_2H.
○: *p*-TsN_2Ph/CF_3CO_2H=5.89 mol/mol
●: *p*-TsN_2Ph/CF_3CO_2H=2.95 mol/mol

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[4] A. H. Blatt, Editor, "Organic Syntheses," Coll. Vol. I, p. 492 (1941).

[5] A. Hantzsch and M. Singer, *Ber.*, **30**, 312 (1897); **31**, 641 (1898).

[6] K. Ishida, N. Kobori, M. Kobayashi and H. Minato, This Bulletin, **43**, 285 (1970).

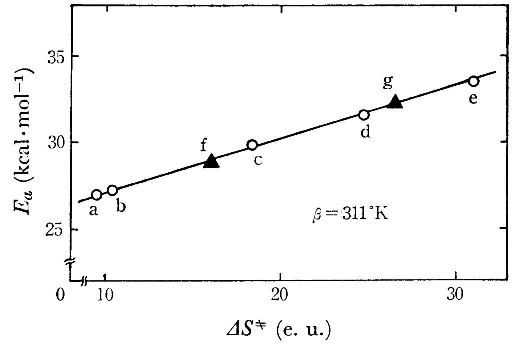
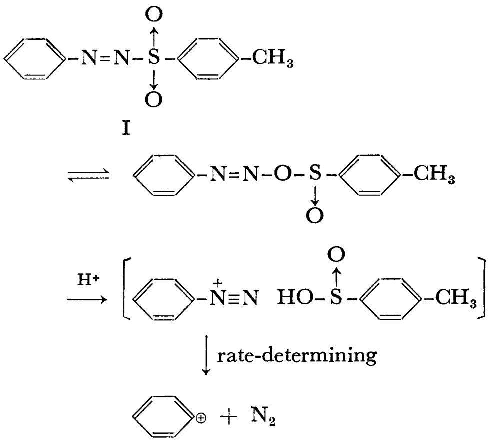


Fig. 3. Isokinetic relationship for the decomposition of PhN_2BF_4 and p-TsN_2Ph in various solvents
○: Decomposition of PhN_2BF_4 in aprotic polar solvents.
(a: $(CH_3)_2C{=}O$, b: DMSO, c: CH_3CN, d: DMF, e: CH_3NO_2)
●: Decomposition of p-TsN_2Ph in benzene-CF_3CO_2H
(f: p-TsN_2Ph/CF_3CO_2H=5.89 mol/mol, g: p-TsN_2Ph/CF_3CO_2H=2.95 mol/mol)

findings, the following mechanism is proposed, in which the generation of phenyl cation from benzenediazonium ion is the rate-determining step. When trifluoroacetic acid was added to a benzene solution of the azosulfone, a new absorption corresponding to $Ar{-}N^+{\equiv}N$ was observed at 2280 cm^{-1}, which gradually disappeared with evolution of nitrogen. This finding is consistent with the above mechanism.

Tables 2 and 3 show the orientation and the partial rate factors for the phenylation of substituted benzenes with the azosulfone in the presence of trifluoroacetic acid. p-Toluenesulfinic acid was not



isolated, but p-toluenesulfonic acid and phenyl p-toluenesulfonate were found. p-Toluenesulfonic acid is ascribable to the disproportionation of p-toluenesulfinic acid, which Kice and his co-workers reported.[7] Products other than the phenylation products will be discussed in a forthcoming paper. When acetonitrile or DMSO was present, acetanilide or 1,3-benzoxathian was formed, as reported in a previous paper.[3]

When the substituent was $-CO_2Me$ or $-NO_2$, in a substituted benzene alone or in a mixture of a substituted benzene and acetonitrile *meta* derivatives predominate and the partial rate factors were much smaller than unity, whereas in a mixture of a substituted benzene and DMSO o,p-derivatives predominate. This abnormality in DMSO-PhX can be ascribed to the ocurrence of both the homolytic and heterolytic decomposition of the azosulfone in this medium, since less protons are available for protonation of the azosulfone owing to the protona-

TABLE 2. ORIENTATION (%) FOR THE PHENYLATION OF PhX WITH p-TsN_2Ph IN ACIDIC SOLUTIONS AT 40°C

X in PhX	Solvents								
	PhX only			CH_3CN-PhX			DMSO-PhX		
	o-	*m*-	*p*-	*o*-	*m*-	*p*-	*o*-	*m*-	*p*-
OCH_3	73.5	5.1	21.4	58.9	11.0	30.1	56.9	20.3	22.8
	76.0	4.8	19.2	59.9	10.2	29.9			
C_2H_5	54.1	21.9	24.0	52.6	25.8	21.6	49.2	27.8	23.0
	53.5	21.5	25.0	48.5	25.6	25.9			
Cl	72.8	6.6	20.6	49.6	19.3	31.1	55.4	17.7	26.9
	70.3	9.4	20.3	52.6	17.8	29.6			
CO_2CH_3	48.8	41.4	9.8	37.0	54.1	8.9	54.2	28.5	17.3
	48.6	42.2	9.2	41.3	48.7	10.0			
NO_2	24.8	70.1	5.1	22.2	48.3	29.5	68.1	17.4	14.5
	27.2	67.8	5.0	21.5	50.0	28.5			

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[7] J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, **84**, 605 (1962); J. L. Kice and G. Guaraldi, *ibid.*, **88**, 5236 (1966); J. L. Kice and G. Guaraldi, *Tetrahedron Lett.*, **1966**, 501.

TABLE 3. PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH *p*-TsN_2Ph IN ACIDIC SOLUTIONS AT 40°C

X in PhX	PhX only			CH_3CN-PhX			DMSO-PhX		
	k_o/k	k_m/k	k_p/k	k_o/k	k_m/k	k_p/k	k_o/k	k_m/k	k_p/k
OCH_3	2.66	0.18	1.55	1.64	0.31	1.68	1.99	0.71	1.59
	2.66	0.17	1.34	1.79	0.30	1.79			
C_2H_5	1.32	0.59	1.17	1.60	0.78	1.31	1.49	0.79	1.30
	1.32	0.53	1.23	1.53	0.81	1.63			
Cl	0.61	0.07	0.35	0.57	0.22	0.72	0.96	0.31	0.94
	0.56	0.08	0.33	0.62	0.21	0.70			
CO_2CH_3	0.48	0.41	0.19	0.59	0.86	0.28	0.96	0.50	0.61
	0.43	0.37	0.16	0.58	0.68	0.28			
NO_2	0.07	0.21	0.03	0.08	0.17	0.21	1.33	0.34	0.57
	0.08	0.19	0.03	0.09	0.21	0.24			

tion of DMSO. Decompositions in a substituted benzene alone or in CH_3CN-PhX will be discussed further in detail.

The orientation and the partial rate factors in PhX or in CH_3CN-PhX are quite different from those for the radical phenylation of substituted benzenes[8] and quite similar to those for phenylation with phenyl cation generated from benzenediazonium tetrafluoroborate.[3,9] The partial rate factors for *meta* and *para* positions in Table 3 are better correlated with σ values of Brown-Okamoto rather than those of Hammett. However, as Fig. 4 shows, the correlation coefficient is rather small, and the reaction constant ρ is very small compared with the ρ values of common electrophilic reactions (in PhX, $\rho=-1.0$, $r=0.84$; in CH_3CN-PhX, $\rho=-0.69$, $r=0.87$). These findings indicate that phenyl cation is highly reactive and unselective, and they are consistent with the suggestions made by Abramovitch and Gadallah[9] and by us,[3] which describe phenyl cation as a diradical cation produced by the transfer of one π-electron to the vacant sp^2 orbital.

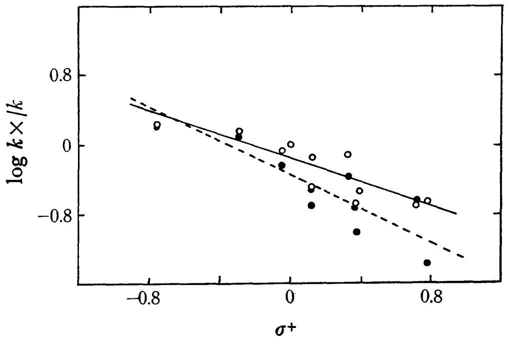
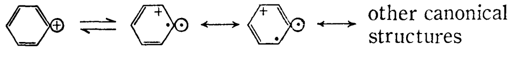
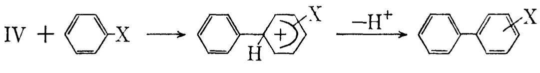


Fig. 4. The Hammett plots for the phenylation with *p*-TsN_2Ph in acidic solutions at 40°C.
—○—: PhX-CH_3CN, $\rho=-0.69$
—●—: PhX only, $\rho=-1.0$

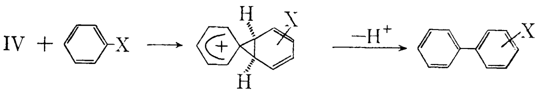


IV IVa IVb

However, at present there is no further evidence available which can determine whether the phenylation proceeds *via* an ordinary σ-complex shown in Scheme 1 or it proceeds *via* a spiro cation shown in Scheme 2.



Scheme 1



Scheme 2

In order to determine whether or not the abstraction of proton from the complex is the rate-determining step, some experiments were performed with deuterated compounds, and the results are shown

TABLE 4. PHENYLATION OF DEUTERATED PhX WITH *p*-TsN_2Ph IN ACIDIC SOLUTIONS AT 40°C

PhX	Orientation (%)			Partial rate factors		
	o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k
$PhOCH_3$-4d	61.9	9.2	28.9			
($PhOCH_3$)	73.5	5.1	21.4			
PhCl-4d	66.1	13.1	20.8			
(PhCl)	70.3	9.4	20.3	0.56	0.08	0.33
PhCl-d_5	63.2	13.4	23.4	0.82	0.17	0.60

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[8] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London (1960); R. Ito, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

[9] R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc., B*, **1968**, 497.

in Table 4. No significant difference in the orientation was found between chlorobenzene-4d and chlorobenzene or between anisole-4d and anisole. The partial rate factors for the phenylation of pentadeuteriochlorobenzene were calculated from a competitive reaction with benzene. The values of k_H/k_D are somewhat smaller than unity, but when experimental errors are taken into consideration, these values are regarded as indicating that there is no isotope effect in phenylation with azosulfone. Therefore, the rate of formation of the complex either in Scheme 1 or Scheme 2 must be much (slower) than the rate of the abstraction of proton from the complex. In the case of spontaneous decomposition of benzenediazonium tetrafluoroborate, the proton-abstracting species is probably DMSO or acetonitrile, whereas in the acid-catalyzed decomposition of the azosulfone the proton abstracting species is probably trifluoroacetate ion. The results of our investigations with benzenediazonium tetrafluoroborate[3] and with phenylazo-*p*-tolylsulfone indicate that regardless of the proton-abstracting species, the abstraction of a proton from the complex must occur very rapidly.

The results of this investigation together with those of Overberger and Rosenthal[1] and those of Bunnet and Happer[2] have established the very interesting features of the decomposition of arylazoarylsulfone, which are summarized as follows. It is of interest to compare the decomposition of the azosulfone with the decomposition of benzenediazonium salts, which yields phenyl radical in an alkaline medium and phenyl cation in an acidic medium.