

Mechanism of Replacement of the Nitro Group and Fluorine Atom in *meta*-Substituted Nitrobenzenes by Phenols in the Presence of Potassium Carbonate

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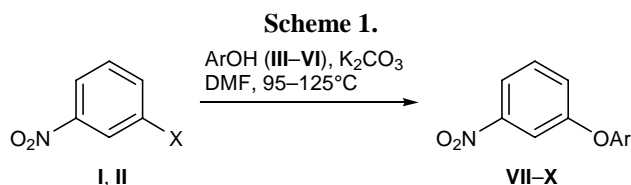
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Abstract—The relative mobilities of the nitro group and fluorine atom in 1,3-dinitrobenzene and 1-fluoro-3-nitrobenzene by the action of phenols in the presence of potassium carbonate in dimethylformamide at 95–125°C were studied by the competing reaction method. The rate constant ratios $k(\text{NO}_2)/k(\text{F})$ were correlated with the differences between the corresponding activation parameters ($\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$). The greater mobility of the nitro group was found to be determined by the entropy control of the reactivity of arenes. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) were calculated, and the enthalpy–entropy compensation effect was revealed. The reaction mechanism is discussed.

Nucleophilic aromatic substitution still remains an extensively developing field of organic chemistry [1, 2] due to diversity of mechanisms of these reactions [1–4] and their wide synthetic potential [5–7]. Nucleophilic substitution of hydrogen ($\text{S}_\text{N}^\text{H}$) in arenes provides an effective tool for their functionalization [1, 2, 8, 9], though replacement of a nucleofugal group in aromatic compounds is equally important. The latter process makes it possible to obtain not only *ortho* or *para* isomers but also *meta*-substituted derivatives with high regioselectivity [1]. *meta*-Substituted arenes are formed most readily by replacement of a halogen atom (Cl, Br, I) in copper- and palladium-catalyzed reactions [10] or of another readily departing group (such as nitro group or fluorine atom) by nucleophilic species generated *in situ* [11–13]. Systematic studies on such reactions were initiated relatively recently [11–13] due to wide prospects in further functionalization of the substrates [11, 14].

Studies on the kinetics of nucleophilic replacement in *meta*-substituted nitrobenzenes by the action of phenols in the presence of potassium carbonate have shown that the dependences of the rate constant on the temperature, reagent nature, and nucleofugality of the leaving group differ considerably [12, 13, 15, 16] from those found for analogous reactions with potassium phenoxides [17–20]. With the goal of elucidating the general relations between the reactant structure and

energy parameters of the reaction, which provide some information on the reaction mechanism, we studied the relative mobilities of the nitro group in 1,3-dinitrobenzene (**I**) and fluorine atom in 1-fluoro-3-nitrobenzene (**II**) in reactions with phenols **III–VI** in DMF in the presence of potassium carbonate (Scheme 1) at different temperatures.



I, X = NO₂; **II**, X = F; **III**, **VII**, Ar = 4-MeC₆H₄; **IV**, **VIII**, Ar = Ph; **V**, **IX**, Ar = 4-ClC₆H₄; **VI**, **X**, Ar = 3-O₂NC₆H₄.

We found that in the temperature range from 95 to 125°C the ratio of the rate constants for replacement of the nitro group and fluorine atom $k(\text{NO}_2)/k(\text{F})$ is greater than unity and that it increases with rise in both temperature and acidity of phenols (Table 1). For each phenol **III–VI**, $\log[k(\text{NO}_2)/k(\text{F})]$ values are linearly related to the reciprocal temperature $1/T$ ($r \geq 0.998$, Fig. 1). Using these relations we calculated the differences between the apparent activation parameters $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ according to the modified Eyring equation (Table 1). The $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values are positive and are linearly related to each other ($r = 0.999$). This

Table 1. Rate constant ratios $k(\text{NO}_2)/k(\text{F})$ for the replacement of nitro group and fluorine atom and differences in the activation parameters for competing reactions of compounds **I** and **II** with phenols **III–VI** in the presence of K_2CO_3 in DMF

Compound no.	$k(\text{NO}_2)/k(\text{F})^a$				$\Delta\Delta H^\ddagger, ^b \text{ kJ/mol}$	$\Delta\Delta S^\ddagger, ^b, ^c \text{ J mol}^{-1} \text{ K}^{-1}$
	98°C	110°C	120°C	125°C		
III	1.06±0.02	1.16±0.01	1.23±0.01	1.03±0.01 ^d	8.5±0.1	23.5±0.3
IV	1.08±0.01	1.21±0.01	1.31±0.01	1.36±0.01	10.5±0.1	28.9±0.3
V	1.12±0.04	1.27±0.02	1.40±0.01	1.48±0.01	12.6±0.4	34.8±1.1
VI	1.90 ^{e, f}	1.79±0.01 ^g	1.54±0.02	1.66±0.02	16.3±0.2	45.0±0.5

^a Average value from no less than two parallel runs.

^b $\Delta\Delta H^\ddagger = \Delta H^\ddagger(\text{NO}_2) - \Delta H^\ddagger(\text{F})$; $\Delta\Delta S^\ddagger = \Delta S^\ddagger(\text{NO}_2) - \Delta S^\ddagger(\text{F})$; calculated by the modified Eyring equation: $\log[k(\text{NO}_2)/k(\text{F})] = (-\Delta\Delta H^\ddagger/T + \Delta\Delta S^\ddagger)/4.576$.

^c At 98°C.

^d At 95°C.

^e At 137°C.

^f Data of [21].

^g At 132°C.

suggests that replacement of the nitro group in **I** by each phenol is favored by the entropy factor and that replacement of the fluorine atom in **II** is favored by the enthalpy factor. As follows from Fig. 1, all competing reactions with phenols **III–VI** are entropy-controlled ($\Delta\Delta H^\ddagger < T\Delta\Delta S^\ddagger$) at a temperature exceeding 90°C.

Comparison of these results with those obtained previously while studying competing reactions of 3,5-dinitrobenzotrifluoride (**XI**) and 3-fluoro-5-nitrobenzotrifluoride (**XII**) with the same phenols (**III–VI**) in the presence of K_2CO_3 in DMF [16] allowed us to estimate the effect of the substrate electrophilicity on the relative mobilities of the nitro group and fluorine atom. Analysis of the dependences $\log[k(\text{NO}_2)/k(\text{F})]-1/T$ (Fig. 1) indicates similarity in the relations observed for *meta*-substituted nitrobenzenes **I** and **II**, on the one hand, and 3-nitrobenzotrifluorides **XI** and **XII**, on the other. However, the sensitivity of $\log[k(\text{NO}_2)/k(\text{F})]$ to temperature and reagent structure considerably increases as the substrate electrophilicity rises.

As with compounds **XI** and **XII** [16], the competing reactions of nitrobenzenes **I** and **II** with phenols **III–VI** fit the Hammett and Brønsted dependences $\log[k(\text{NO}_2)/k(\text{F})]-\sigma(\text{p}K_a)$ (Table 2). Here, the positive differences in the ρ values, $\Delta\rho = \rho(\text{NO}_2) - \rho(\text{F})$, and negative differences in the Brønsted coefficients, $\rho\beta_{\text{Nu}} = \beta_{\text{Nu}}(\text{NO}_2) - \beta_{\text{Nu}}(\text{F})$, are linear in $1/T$ (Table 3). The data in Table 3 show that the isokinetic temperatures β calculated from different dependences fall into a narrow range; therefore, reactions of phenols **III–VI** with compounds **I** and **II** can be regarded as a reaction series for which isoselective relationship is fulfilled [25].

It is known that isoselective relationship exists when the isokinetic temperatures for two reaction series are equal [26]. Therefore, the replacement of both nitro group in **I** and fluorine atom in **II** by the action of phenols **III–VI** in the presence of K_2CO_3 gives rise to isokinetic relationship with $\beta = 361 \text{ K}$. Insofar as an isokinetic series is characterized by the equation [27]

$$-2.303RT\rho\sigma = (\beta - T)\delta\Delta S^\ddagger = (1 - T/\beta)\delta\Delta H^\ddagger,$$

the activation parameters are linearly related to the substituent constants σ in ArOH :

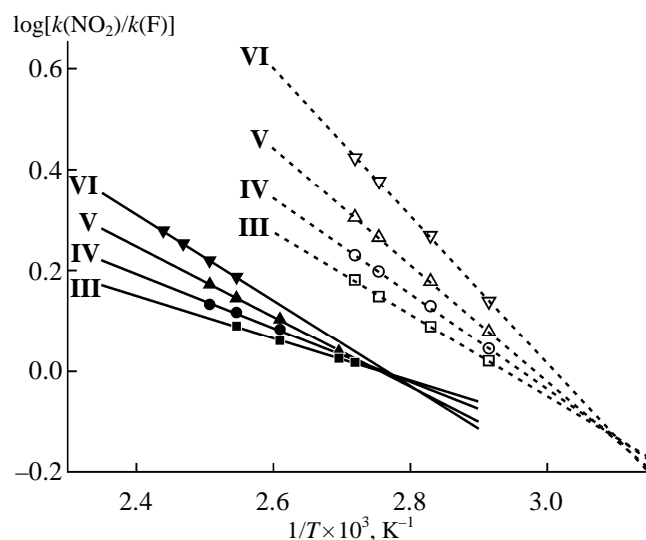


Fig. 1. Plots of $\log[k(\text{NO}_2)/k(\text{F})]$ versus $1/T$ for competing reactions of compounds **I** and **II** with phenols **III–VI** in the presence of K_2CO_3 in DMF (solid lines). For comparison, analogous plots are given for competing reactions of compounds **XI** and **XII** with the same phenols in the presence of K_2CO_3 in DMF [16] (dashed lines).

Table 2. Parameters of the Hammett and Brønsted equations $\log[k(\text{NO}_2)/k(\text{F})] = \Delta\rho\sigma + a$ and $\log[k(\text{NO}_2)/k(\text{F})] = \Delta\beta_{\text{Nu}}\rho K_a + b$ for competing reactions of compounds **I** and **II** with phenols **III–VI** in the presence of K_2CO_3 in DMF^a

Parameter	Temperature, °C			
	98	110	120	125
$\Delta\rho$	0.041	0.075	0.108	0.129
a	0.034	0.081	0.114	0.133
r	0.973	0.989	0.990	0.993
s	0.008	0.007	0.006	0.005
$\Delta\beta_{\text{Nu}}$	-0.008	-0.015	-0.022	-0.026
b	0.191	0.369	0.531	0.627
r	0.978	0.992	0.993	0.995
s	0.008	0.006	0.005	0.004

^a The ratios $k(\text{NO}_2)/k(\text{F})$ were taken from Table 1; $\sigma_p^- = -0.17$ (4-Me), 0 (H), 0.19 (4-Cl), $\sigma_m = 0.71$ (3-NO₂) [22]; $\text{p}K_a$ of phenols in DMSO: 18.9 (**III**), 18.0 (**IV**), 16.75 (**V**), 14.4 (**VI**) [23]; $\text{p}K_a$ values of phenols in DMF are related to $\text{p}K_a$ in DMSO by the formula: $\text{p}K_a(\text{DMF}) = 1.56 + 0.96\text{p}K_a(\text{DMSO})$ [24].

Table 3. Isokinetic temperatures β calculated from different dependences^a

Dependence	β , K	r	s
$\Delta\Delta H^\ddagger = f(\Delta\Delta S^\ddagger)$	362 ± 1	0.999	0.024
$\log[k(\text{NO}_2)/k(\text{F})] = f(1/T)$	359 ± 3		
$\Delta\rho = f(1/T)$	361 ± 2	0.996	0.004
$\Delta\beta_{\text{Nu}} = f(1/T)$	361 ± 2	0.997	0.001

^a The values of $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ were taken from Table 1, and $\Delta\rho$ and $\Delta\beta_{\text{Nu}}$, from Table 2.

Table 4. Parameters of the $\delta\Delta H^\ddagger = \beta c\sigma$ and $\delta\Delta S^\ddagger = c\sigma$ dependences for replacement of the nitro group in compounds **I** and **XI** and fluorine atom in **II** and **XII** by the action of phenols **III–VI** in the presence of K_2CO_3 in DMF

Comp. no.	ρ (temperature, K)	β , K	Parameter	
			c , J mol ⁻¹ K ⁻¹	βc , kJ/mol
I	-1.638 ^a (423)	361	-214	-77
II	-1.835 ^b (423)		-240	-87
XI	-0.675 ^c (343)	322 ^d	-211	-68
XII	-0.809 ^e (343)		-253	-81

^a Data of [15].

^b $\rho(\text{F}) = \rho(\text{NO}_2) - \Delta\rho$; $\Delta\rho = 0.197$ at 423 K; calculated from the dependence $\Delta\rho = f(1/T)$ (Table 3).

^c Data of this work.

^d $\rho(\text{F}) = \rho(\text{NO}_2) - \Delta\rho$; $\Delta\rho = 0.134$ at 343 K [16].

^e Data of [16].

$$\delta\Delta S^\ddagger = c\sigma \text{ and } \delta\Delta H^\ddagger = \beta c\sigma,$$

where $c = -2.303RT\rho/(\beta - T)$. Using our results and previously reported data [15, 16] we can calculate the parameters c and βc for each substrate in the reaction with phenols **III–VI** in the presence of K_2CO_3 (Table 4). As follows from Table 4, these parameters have large negative values reflecting a high sensitivity of ΔH^\ddagger and ΔS^\ddagger to the substituent nature in ArOH; they also depend on the nature of the leaving group and substrate electrophilicity.

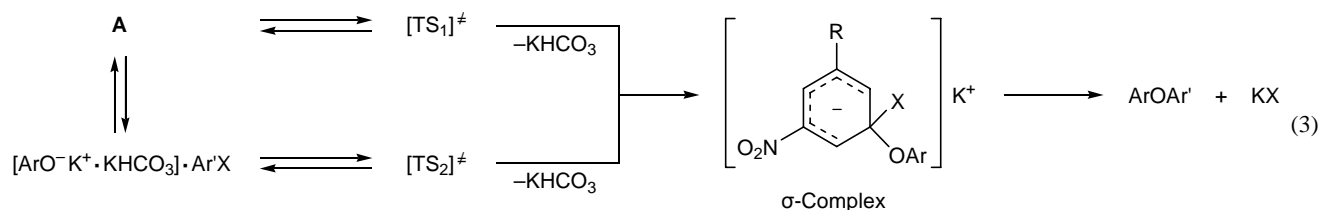
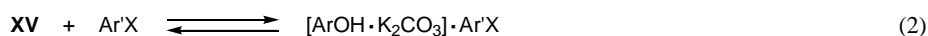
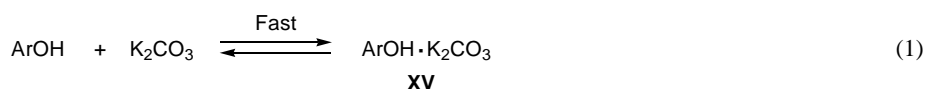
Using the activation parameters ΔH^\ddagger and ΔS^\ddagger determined previously for the reaction of compound **I** with 3,4-dimethylphenol (**XIII**) in DMF in the presence of K_2CO_3 [15] and the values of c and βc (Table 4), we calculated ΔH^\ddagger and ΔS^\ddagger for the reactions of **I** with phenols **III–VI** (Table 5). The obtained data together with the $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values (Table 1) were then used to determine the corresponding values for the reactions of 1-fluoro-3-nitrobenzene (**II**) with the same phenols (Table 5). Table 5 also contains the activation parameters for the reactions of compounds **XI** and **XII** with phenols **III–VI** in DMF in the presence of K_2CO_3 , which were calculated as described above from ΔH^\ddagger and ΔS^\ddagger for the reaction of **XII** with 4-chlorophenol (**V**).

Our results are sufficiently reliable, as follows from comparison of the calculated (Table 5) and experimental [28] relative rate constants of the competing reactions of compounds **I** and **XI** with 4-bromophenol (**XIV**) in DMF in the presence of K_2CO_3 at 100°C: $k(\text{XI})/k(\text{I}) = 148$ and 151, respectively.

The observed general relations between structural factors and activation parameters (Tables 1, 5) led us to conclude that under the given conditions ($\beta < T$) the kinetics of each reaction, as well as the effect of substituent in the substrate, are determined by the enthalpy factors and that the effects of the leaving group in the substrate and of the substituent in the reagent are determined by the entropy factors.

The enthalpy and entropy of activation in the replacement of nitro group and fluorine atom in *meta*-substituted nitrobenzenes **I**, **II**, **XI**, and **XII** by the action of phenols **III–VI** in the presence of K_2CO_3 range from 126 to 233 kJ/mol and from -18 to 255 J mol⁻¹ K⁻¹, respectively (Table 5). These data contradict the concept involving formation of a σ -complex in the framework of the classical S_NAr mechanism [17]. On the other hand, the Gibbs energies of activation for all the examined reactions (120–

Scheme 2.



140 kJ/mol) approach the ΔG^\ddagger range typical of S_N reactions of weakly activated arenes with charged O-nucleophiles [17]. Figure 2 shows two compensation (isokinetic) dependences, one of which corresponds to the reactions with compounds **I** and **II**, and the other, to the reactions with **XI** and **XII**.

It should be emphasized that anomalously broad ranges of variation of the enthalpy and entropy of activation, for which isokinetic relationship is fulfilled, are typical of complex heterogeneous and enzymatic catalytic reactions [29]. Therefore, we propose a refined scheme for S_N reactions of *meta*-substituted arenes with phenols in the presence of K_2CO_3 (Scheme 2, cf. [16]). The first stage [reaction (1)] is fast formation of complex **XV** [16] which then reacts with substrate to give complex **A** via intermolecular interactions [reaction (2)] (cf. [30]). Complex **A** undergoes intramolecular transformation (either in a synchronous mode through transition state TS_1 or in a stepwise mode through transition state TS_2) leading to σ -complex [reaction (3)]. According to the proposed kinetic scheme, the apparent rate constant characterizes the stage of formation of σ -complex and the preceding stage. Taking into account the calculated isokinetic temperatures which are typical of equilibrium formation of complexes like **A** [31], we presume that the high sensitivity of the activation parameters to the reagent structure is determined mainly by reaction (2). Obviously, a necessary condition is the possibility for complex **XV** to considerably change its geometry upon interaction with $\text{Ar}'\text{X}$. We previously showed [32] that reactions of phenols with potassium carbonate in dipolar aprotic solvents give at least two types of complexes, including $(2\text{ArOH}) \cdot \text{K}_2\text{CO}_3$ for which equilibrium structures were determined [32]. Presumably, just the ability of the $(2\text{ArOH}) \cdot \text{K}_2\text{CO}_3$ complex to change its structure is responsible for some similar-

ity between S_N reactions of *meta*-substituted arenes with phenols in the presence of K_2CO_3 and heterogeneous or enzymatic processes.

The existence of an isoselective relationship indicates that the structure of complex **A** depends on the substrate electrophilicity rather than on the nature of the leaving group. In this case, the isotope effect, i.e., the dependence of the substitution selectivity in competing reactions of compounds **XI** and **XII** with phenols **III** and **VI** in the presence of K_2CO_3 at 70°C on the isotope composition of the reagent S_H/S_D (Table 6), is controlled by stage (3).

Thus analysis of empirical correlations found for S_N reactions of *meta*-substituted nitrobenzenes with

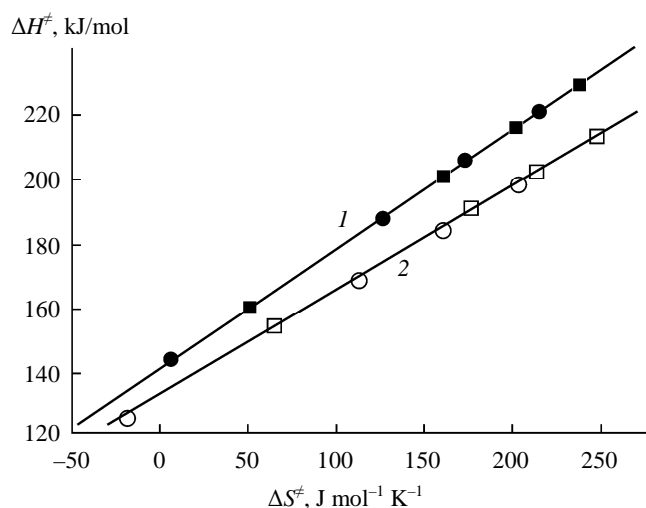


Fig. 2. Isokinetic relationships (ΔH^\ddagger versus ΔS^\ddagger) for (1) nucleophilic replacement of the nitro group in compound **I** and fluorine atom in **II** ($\Delta H^\ddagger = 0.36\Delta S^\ddagger + 141$, $r = 0.999$, $n = 8$, $s = 0.3$) and (2) analogous reactions of compounds **XI** and **XII** ($\Delta H^\ddagger = 0.32\Delta S^\ddagger + 132$, $r = 0.999$, $n = 8$, $s = 0.7$) with phenols **III**–**VI** in the presence of K_2CO_3 in DMF (the ΔH^\ddagger and ΔS^\ddagger values were taken from Table 5).

Table 5. Activation parameters for replacement of the nitro group in compounds **I** and **XI** and fluorine atom in **II** and **XII** by the action of phenols **III–VI**, **XIII**, and **XIV** in the presence of K_2CO_3 in DMF

Substrate	Phenol	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , J mol ⁻¹ K ⁻¹
I ^a	XIII	233	255
	III	228	240
	IV	215	204
	V	200	163
	VI	160	52
	XIV	195	150
II ^b	III	220	217
	IV	205	175
	V	187	128
	VI	144	7
XI ^c	III	212	250
	IV	201	215
	V	190	178
	VI	154	66
XII	XIV ^f	184	162
	III ^d	197	205
	IV ^d	183	162
	V ^e	168	114
	VI ^d	126	-18

^a The ΔH^\ddagger and ΔS^\ddagger values for the reactions with 1,3-dinitrobenzene (**I**) were calculated by the equations $\Delta H^\ddagger = 233 - \beta c \Delta\sigma$ and $\Delta S^\ddagger = 255 - c \Delta\sigma$, where 233 J/mol and 255 J mol⁻¹ K⁻¹ are the corresponding activation parameters for the reaction of **I** with 3,4-dimethylphenol (**XIII**) [15], and $\Delta\sigma$ is the difference between the substituent constants in 3,4-dimethylphenol and phenols **III–VI** [22].

^b The ΔH^\ddagger and ΔS^\ddagger values for the reactions with 1-fluoro-3-nitrobenzene (**II**) were determined from the corresponding parameters for compound **I** and $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values (Table 1).

^c The ΔH^\ddagger and ΔS^\ddagger values for the reactions with compound **XI** were determined from the sum of the activation parameters for the reactions with **XII** and $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values for competing reactions of compounds **XI** and **XII** [16].

^d The ΔH^\ddagger and ΔS^\ddagger values for the reactions of compound **XII** with phenols **III**, **IV**, and **VI** were calculated by the equations $\Delta H^\ddagger = 168 + \beta c \Delta\sigma$ and $\Delta S^\ddagger = 114 + c \Delta\sigma$, where 168 kJ/mol and 114 J mol⁻¹ K⁻¹ are the corresponding activation parameters for the reaction of **XII** with phenol **V**, and $\Delta\sigma$ is the difference between the substituent constants in 4-chlorophenol (**V**) and phenols **III**, **IV**, and **VI**.

^e The ΔH^\ddagger and ΔS^\ddagger values for the reaction of compound **XII** with phenol **V** were determined from the sum of the activation parameters for the reaction with **II** and $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ values (see Experimental).

^f The ΔH^\ddagger and ΔS^\ddagger values for the reaction of compound **XI** with 4-bromophenol (**XIV**) were extrapolated from the dependences $\Delta H^\ddagger = f(\sigma)$ and $\Delta S^\ddagger = f(\sigma)$ for the reactions of **XI** with phenols **III–VI**.

phenols in the presence of K_2CO_3 revealed crucial role of molecular organization of the reagents under the conditions of nucleophile generation *in situ* (cf. [33]).

EXPERIMENTAL

The reaction mixtures were analyzed by GLC on an LKhM-72 chromatograph equipped with a thermal conductivity detector; 4000×4-mm column, stationary phase 15% of SKTFT-803 on Chromaton-W; linear oven temperature programming from 70 to 270°C at a rate of 10 deg/min; carrier gas helium. The components were quantitated by absolute calibration using calibration curves and were identified by adding authentic samples.

Commercial dimethylformamide was dried over 4-Å molecular sieves and was distilled over calcium hydride under reduced pressure. Commercial phenols **III–VI** were purified by standard procedures. Commercial potassium carbonate of analytical grade was dehydrated by heating in a muffle furnace for 3 h at 400°C, finely ground, and additionally dried by heating for 2 h at 150°C under reduced pressure (~5 mm). Commercial 1,3-dinitrobenzene (**I**) and 1-fluoro-3-nitrobenzene (**II**) were purified by standard procedures. 3,5-Dinitrobenzotrifluoride (**XI**), mp 47–48°C, and 3-fluoro-5-nitrobenzotrifluoride (**XII**), bp 67–68°C (4 mm), were synthesized as described in [34]; their physical constants were in agreement with published data. Deuterated phenols ArOD (**III** and **VI**) were prepared by the procedure reported in [35]. Compounds **VII–X** used as authentic samples were synthesized as described in [21].

The general procedures for carrying out competing reactions and treatment of the results were reported previously [16, 28]. The data obtained for competing reactions of compounds **I** and **II** with phenols **III–VI** in DMF in the presence of DMF at 95–125°C are given in Table 1. From the data obtained for competing reactions of phenols **III–VI** with compound **XI** in the presence of K_2CO_3 in DMF at 70°C [$k(\text{III})/k(\text{IV}) = 1.26 \pm 0.05$, $k(\text{V})/k(\text{IV}) = 0.81 \pm 0.03$, $k(\text{VI})/k(\text{IV}) = 0.32 \pm 0.02$] we calculated $\rho(\text{NO}_2) = -0.675$. From the data obtained for competing reactions of compounds **I** and **XII** with 4-chlorophenol (**V**) in the presence of K_2CO_3 in DMF at 130–145°C [$k(\text{XII})/k(\text{I}) = 55 \pm 2$, 130°C; 50 ± 1 , 135°C; 47 ± 2 , 140°C; 45 ± 1 , 145°C] we calculated the differences in the enthalpies and entropies of activation: $\delta\Delta H^\ddagger = \Delta H^\ddagger(\text{XII}) - \Delta H^\ddagger(\text{I}) = -19$ kJ/mol and $\delta\Delta S^\ddagger = \Delta S^\ddagger(\text{XII}) - \Delta S^\ddagger(\text{I}) = -14$ J mol⁻¹ K⁻¹. The data obtained for competing

Table 6. Isotope effect on the selectivity of replacement of the nitro group and fluorine atom (S_H/S_D) in reactions of compounds **XI** and **XII** with phenols **III** and **VI** in the presence of K_2CO_3 at 70°C in DMF

Comp. no.	$S_H = k^H(NO_2)/k^H(F)^a$	$S_D = k^D(NO_2)/k^D(F)^b$	S_H/S_D
III	1.05±0.05	0.84±0.01	1.25
VI	1.38±0.02	1.26±0.03	1.10

^a Data of [16].

^b Average value from at least two parallel runs.

reactions of compounds **XI** and **XII** with deuterated phenols ArOD (**III**, **VI**) in the presence of K_2CO_3 in DMF are given in Table 6.

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