===

Effect of the Nucleophile Structure on the Relative Mobility of the Nitro Group and Fluorine Atom in Reactions of 3,5-Dinitro- and 3-Fluoro-5-nitrobenzotrifluorides with Phenols in the Presence of Potassium Carbonate*

I. A. Khalfina and V. M. Vlasov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,
pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia

Abstract—The relative mobility of the nitro group and fluorine atom in 3,5-dinitro- and 3-fluoro-5-nitro-benzofluorides was estimated by the competing reaction technique using phenols in the presence of potassium carbonate (DMF, 65–95°C). Correlation analysis of the relative rate constants $k(NO_2)/k(F)$ and of the differences in the activation parameters ($\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$) of competing reactions showed the existence of two reaction series for the examined phenols. The higher mobility of the nitro group was found to result from the entropy control of the reactivity of arenes. The mechanism of these reactions is discussed.

It is known [1, 2] that *ipso*-substitution in $S_N Ar$ reactions of *meta*-substituted nitrobenzenes with various charged nucleophiles becomes possible due to high mobility of the nitro group and fluorine atom, whose reactivities are comparable [3]. However, such reactions are fairly rare cases [1, 2, 4–10] because of not only insufficient substrate activation but also the existence of equilibrium between different kinds of σ-complexes [10, 11]. As a result, $S_N Ar$-replacement of the nitro group or fluorine atom in *meta*-substituted nitrobenzenes in reactions with various nucleophiles usually requires drastic conditions, the yields of the target products are low, and the process is accompanied by side reactions [5, 6, 9]. Phenoxide ions are among such nucleophiles, and substitution reactions with participation of phenoxide ions can be complicated by formation of C-arylation products [10, 12]. As was shown in [13–16], phenols smoothly react with *meta*-substituted nitrobenzene derivatives in dipolar aprotic solvents in the presence of alkali metal carbonates, yielding products of replacement of the nitro group by phenoxy. The proposed reaction scheme includes preliminary chemisorption of the reactants on the surface of deprotonating agent, the

subsequent $S_N Ar$ reaction, and desorption of the products [17, 18]. Clearly, such heterogeneous processes are difficult to study by direct kinetic methods. On the other hand, the competing reaction technique may be useful for studying substrates possessing comparable reactivities, since the apparent reaction rate should weakly depend on the rates of particular stages other than the replacement stage [19]. As applied to heterogeneous processes, the competing reaction technique makes it possible to estimate the effect of nucleofuge on the substrate reactivity with regard to phenol structure; also, the series of appropriate nucleophiles can be extended. The choice of a nitro group and fluorine atom as a couple of nucleofuges for competing reactions ensures mild conditions of the substitution. We showed in [15] that 1,3-dinitro- and 1-fluoro-3-nitrobenzenes react with phenol and 3-nitrophenol in DMF in the presence of K_2CO_3 under fairly mild conditions to give the corresponding products in almost quantitative yields; it was also found that the mobilities of the nitro group and fluorine atom in competing reactions are comparable. In the present work, using the competing reaction technique, we have studied the relative reactivity of the nitro group in 3,5-dinitrobenzotrifluoride (**I**) and of the fluorine atom in 3-fluoro-5-nitrobenzotrifluoride (**II**) toward phenols **III–IX** whose acidity varies over a wide range. The reactions were carried out in DMF in the presence of

Scheme 1.
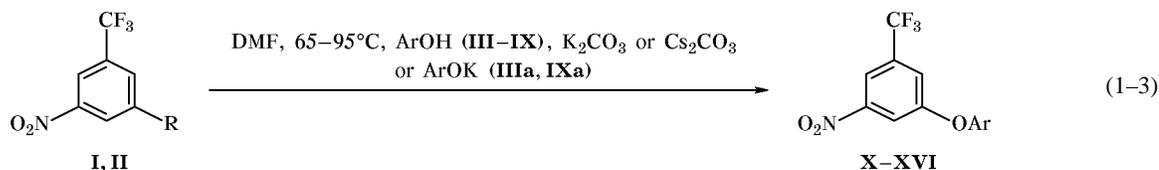
I, R = NO$_2$ [reaction (1)]; II, R = F [reaction (2)]; R = NO$_2$/F [competing reactions (3)]; III, IIIa, X, Ar = 4-MeC$_6$H$_4$; IV, XI, Ar = Ph; V, XII, R = 4-ClC$_6$H$_4$; VI, XIII, R = 3-NO$_2$C$_6$H$_4$; VII, XIV, R = 4-AcC$_6$H$_4$; VIII, XV, R = 4-NCC$_6$H$_4$; IX, IXa, XVI, R = 3-NO$_2$-5-BrC$_6$H$_3$.

K$_2$CO$_3$ in the temperature range from 65 to 95°C (Table 1). In addition, we have determined the relative rate constants for replacement of the nitro group and fluorine atom in compounds I and II in reactions with weakly and strongly acidic phenols (compounds III and IX) in the presence of potassium and cesium carbonates (heterogeneous conditions) and with potassium phenoxides IIIa and IXa (homogeneous conditions) in DMF with the goal of estimating the effect of adsorption on the reaction kinetics.

The selected temperature range ensured quantitative yields of the target products and the absence of by-products. For example, competing reaction (3) with phenols III–VI above 98°C or with phenols VII–IX above 80°C resulted in formation of 3,3′-dinitro-5,5′-bis(trifluoromethyl)diphenyl ether (XVII) as by-product (see Experimental) via reaction of I and II with the released ambient nitrite ion. The latter is known to compete with phenoxide ions at elevated temperature [16, 20].

Electron-acceptor substituents in the substrate are known to accelerate replacement of the nitro group in *meta*-activated nitro compounds by the action of phenols in DMF in the presence of potassium carbonate [18, 21, 22]. Introduction of electron-donor substituents into the aromatic ring of phenols accelerates reactions (1) and (2) (see Experimental). These facts indicate that the rate-determining stage is formation of σ-complex. The data in Table 1 show that the $k(NO_2)/k(F)$ ratio is greater than unity and that it

Table 1. Relative rate constants $k(NO_2)/k(F)$ and differences in the activation parameters of competing reactions of compounds I and II with phenols III–IX in the presence of K$_2$CO$_3$ (Cs$_2$CO$_3$) and with potassium phenoxides IIIa and IXa in DMF

Comp. no.	$k(NO_2)/k(F)^a$						$\Delta\Delta H^{\neq},^b$ kJ/mol	$\Delta\Delta S^{\neq},^b$ J mol^{-1} K^{-1}
	65°C	70°C	75°C	80°C	90°C	95°C		
III	–	1.05 ±0.05	–	1.23 ±0.06	1.41 ±0.05	1.52 ±0.04	15.4 ±0.2	45.3 ±0.6
III^c	–	1.05 ±0.03	–	–	–	1.50 ±0.03	–	–
IIIa	–	–	–	1.06 ±0.03	1.00 ±0.02	–	–	–
IV	–	1.11 ±0.01	–	1.35 ±0.02	1.58 ±0.01	1.70 ±0.02	18.1 ±0.5	52.9 ±1.4
V	–	1.20 ±0.01	–	1.51 ±0.02	1.84 ±0.01	2.02 ±0.02	21.8 ±0.4	64.0 ±1.2
VI	–	1.38 ±0.02	–	1.86 ±0.02	2.39 ±0.02	2.66 ±0.06	27.6 ±0.8	83.6 ±2.5
VII	1.04 ±0.04	1.53 ±0.02	2.24 ±0.02	3.23 ±0.02	d	d	75.0 ±0.4	225.5 ±0.6
VIII	1.05 ±0.05	1.58 ±0.02	2.34 ±0.01	3.55 ±0.05	d	d	80.3 ±1.1	241.3 ±3.4
IX	1.05 ±0.01	1.66 ±0.02	2.54 ±0.01	4.25 ±0.01	d	d	91.6 ±6.2	275.3 ±9.4
IX^c	–	–	e	2.29 ±0.01	3.72 ±0.02	–	–	–
IXa	–	–	–	e	2.50 ±0.05	2.40 ±0.01	–	–

^{a} Average value from no less than two parallel runs.
^{b} The differences in the activation parameters for competing reaction (3) $\Delta\Delta H^{\neq} = \Delta H^{\neq}(NO_2) - \Delta H^{\neq}(F)$ and $\Delta\Delta S^{\neq} = \Delta S^{\neq}(NO_2) - \Delta S^{\neq}(F)$ were calculated by the Eyring equation: $\log[k(NO_2)/k(F)] = (-\Delta\Delta H^{\neq}/T + \Delta\Delta S^{\neq})/4.576$ [23].
^{c} In the presence of Cs$_2$CO$_3$.
^{d} When the reaction time was 3 h, compound XVII was formed as by-product (see Experimental).
^{e} The relative rate constant was not determined because of the low rate of formation of product XVI (see Experimental).

increases both as the temperature rises and as the acidity of phenols **III–IX** increases. The phenols under study give rise to linear relations between $\log[k(NO_2)/k(F)]$ and $1/T$ ($r = 0.999$) (Fig. 1), which means that the Arrhenius equation is valid for reactions (1) and (2). Taking into account that nucleophilic substitution in compounds **I** and **II** by the action of phenols in the presence of potassium carbonate is a multistage process, the fulfilment of the Arrhenius equation for competing reactions (3) indicates that the ratio of rates of replacement of the nitro group and fluorine atom is determined by the effective rate constants of reactions (1) and (2).

As follows from Fig. 1, the isoselective temperature T_{iso} at which the rate constants of reactions (1) and (2) are equal [$k(NO_2) = k(F)$] is below the experimental temperature range ($T_{exp} > T_{iso}$) for all the examined phenols: $T_{iso} = 42–69°C$ for weakly acid phenols **III–VI** and $T_{iso} = 63–64°C$ for strongly acid phenols **VII–IX**. In keeping with the generally accepted views on the relations between internal (enthalpy) and external (entropy) reactivity factors [24], the nitro group is more reactive than fluorine atom in competing reactions (3) under conditions of entropy control. Therefore, the difference in the effective activation parameters ($\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$) can be calculated by the modified Eyring equation for competing reactions. The $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values thus obtained (Table 1) are linearly related with each other ($r = 0.999$; Table 2); this indicates that isokinetic relationship should be observed for the whole series of phenols **III–IX**. The isokinetic temperature β (i.e., the slope of the linear dependence between $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$) is equal to 331 K (Table 2). The positive sign of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ for reaction (3) (Table 1) suggests that the substitution of the nitro group in **I** is favored by the entropy factor while the substitution of the fluorine atom in **II** is favored by the enthalpy factor. Here, the effects of these factors become stronger as the acidity of phenol increases.

Despite the existence of a common linear relation between $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$, phenols **III–IX** can be divided into two series differing by the values of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$. Phenols **III–VI** are characterized by considerably smaller $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values, as compared to **VII–IX** (Table 1). The same division follows from Fig. 1: the pair cross points of the dependences $\log[k(NO_2)/k(F)] = f(1/T)$ for phenols **III–VI** are located at 322 ± 2 K, whereas the corresponding points for phenols **VII–IX** are located at 338 ± 1 K (Table 2). In reactions with weakly acidic phenols the relative mobility of the nitro group and fluorine atom increases with rise in temperature at
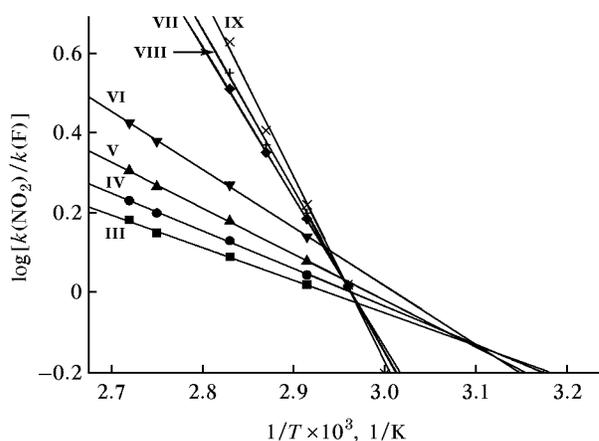
Fig. 1. Plots of $\log[k(NO_2)/k(F)]$ versus $1/T$ for reactions (3) with phenols **III–IX** in the presence of K_2CO_3.

a lower rate than in reactions with phenols of the second series, which are more acidic. The same tendency is observed for the $\log[k(NO_2)/k(F)]–\sigma$ (or pK_a) relations, since the Hammett and Brønsted equations for competing reactions (3) are valid for each phenol series (**III–VI** and **VII–IX**) separately (Table 3). The resulting $\log[k(NO_2)/k(F)]–\sigma(pK_a)$ dependences for all phenols have a V-like shape with equal $\Delta\rho$ ($\Delta\beta_{Nuc}$) values for both branches, which indicates some perturbation of the mechanism of reaction (1) and/or (2) in going from phenols **III–VI** to **VII–IX** [28].

The positive values of $\Delta\rho$ and negative values of the difference in the Brønsted coefficients $\Delta\beta_{Nuc}$ [at $\beta_{Nuc}(NO_2) > 0$ and $\beta_{Nuc}(F) > 0$] throughout the examined temperature range (Table 3) suggest greater sensitivity of the replacement of fluorine atom to

Table 2. Isokinetic temperatures β calculated from different dependences

Dependence	β, K	r	s	n
$\Delta\Delta H^{\neq} = f(\Delta\Delta S^{\neq})$	331 ± 1	0.999	0.250	7
	317 ± 1[a]	0.999	0.266	4
	333 ± 1[b]	0.999	0.333	3
$\log[k(NO_2)/k(F)] = f(1/T)$	322 ± 2[a]			4
	338 ± 1[b]			3
$\Delta\rho = f(1/T)$	322 ± 1[a]	0.998	0.005	4
	338 ± 1[b]	0.960	0.062	4
$\Delta\beta_{Nuc} = f(1/T)$	322 ± 1[a]	0.997	0.001	4
	338 ± 1[b]	0.963	0.009	3

[a] Phenols **III–VI**.
[b] Phenols **VII–IX**.

Table 3. Parameters of the Hammett $\{\lg[k(NO_2)/k(F)] = \Delta\rho\,\sigma + a\}$ and Brønsted equations $\{\log[k(NO_2)/k(F)] = \Delta\beta_{Nuc}- pK_a + b\}$ for competing reactions (3) in the presence of K_2CO_3[a]

Parameter	65°C	70°C	75°C	80°C	90°C	95°C
$\Delta\rho$[b]	–	0.134 ± 0.006	–	0.202 ± 0.013	0.259 ± 0.019	0.276 ± 0.022
$\Delta\rho$[c]	0.017 ± 0.007	0.130 ± 0.03	0.200 ± 0.06	0.44 ± 0.14	–	–
a[b]	–	0.047	–	0.130	0.200	0.235
a[c]	0.003	0.07	0.180	0.130	–	–
r[b]	–	0.996	–	0.995	0.994	0.994
r[c]	0.924	0.968	0.953	0.952	–	–
s[b]	–	0.006	–	0.009	0.013	0.014
s[c]	0.001	0.006	0.010	0.030	–	–
$\Delta\beta_{Nuc}$[b]	–	-0.0264 ± 1	–	-0.040 ± 0.001	-0.051 ± 0.001	-0.054 ± 0.001
$\Delta\beta_{Nuc}$[c]	-0.0021 ± 0.005	-0.020 ± 0.001	-0.031 ± 0.003	-0.067 ± 0.008	–	–
b[b]	–	0.520	–	0.841	1.110	1.207
b[c]	0.048	0.460	0.78	1.439	–	–
r[b]	–	0.999	–	0.999	0.999	0.999
r[c]	0.832	0.998	0.994	0.994	–	–
s[b]	–	0.001	–	0.003	0.004	0.005
s[c]	0.002	0.001	0.004	0.01	–	–

[a] The relative rate constants $k(NO_2)/k(F)$ were taken from Table 1; $\sigma_p^- = -0.17$ (4-CH$_3$), 0 (H), 0.19 (4-Cl), 0.84 (4-Ac), 1.00 (4-CN); $\sigma_m = 0.71$ (3-NO$_2$), 1.10 (3-NO$_2$-5-Br) [25]; pK_a of phenols **III–IX** in DMSO: 18.9 (4-CH$_3$), 18.0 (H), 16.75 (4-Cl), 14.4 (3-NO$_2$), 14.0 (4-Ac), 13.2 (4-CN), 12.2 (3-NO$_2$-5-Br) [26]; pK_a values of phenols in DMF correlate with pK_a in DMSO by the equation pK_a(DMF) = 1.56 + 0.96 pK_a(DMSO) [27].

[b] Phenols **III–VI**.

[c] Phenols **VII–IX**.

the substituent in phenol, as compared to the replacement of nitro group. This trend becomes stronger in reactions of **I** and **II** with more acidic phenols **VII–IX**. The transition state in the stage of formation of σ-complex in the reactions of **II** with phenols in the

Fig. 2. Plots of $-\Delta\beta_{Nuc}$ versus $1/T$ for reaction (3) with phenols (*1*) **III–VI** and (*2*) **VII–IX** in the presence of potassium carbonate.

presence of potassium carbonate is later than in the reactions of compound **I** [29]. Both phenol series conform to the reactivity–selectivity principle, according to which the selectivity of substitution of the nitro group increases as the reactivity of phenoxide ion decreases [30].

The parameters $\Delta\rho$ and $-\Delta\beta_{Nuc}$ for competing reaction (3) increase as the temperature rises, exhibiting a linear relation with $1/T$ for each phenol series (Table 3, Fig. 2). The isokinetic temperatures calculated from the dependence $\Delta\rho$(or $-\Delta\beta_{Nuc}$)–$1/T$ are as follows: $\beta_1 = 322$ K (phenols **III–VI**) and $\beta_2 = 338$ K (phenols **VII–IX**) (Table 2, Fig. 2).

Thus the existence of linear $\Delta\Delta H^{\neq}$–$\Delta\Delta S^{\neq}$ relations implies a common isokinetic relationship for all phenols **III–IX**; however, analysis of the dependences $\log[k(NO_2)/k(F)]$–$1/T$ and $\Delta\rho$(or $-\Delta\beta_{Nuc}$)–$1/T$ led us to distinguish two phenol series, **III–VI** and **VII–IX**, each having its own isokinetic relationship. This discrepancy can be eliminated by analyzing the relations between $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ for each phenol series. Calculation of the isokinetic temperatures gave the values $\beta_1 = 317$ K for phenols **III–VI** and

$\beta_2 = 333$ K for phenols **VII–IX** (Table 2, Fig. 3). We can conclude that a combination of known methods for identification of isokinetic relationships yields consistent results [28], since all β values satisfactorily agree with each other (Table 2).

It should be noted that the existence of isokinetic relationship for reaction (3) implies that isokinetic relationships for reactions (1) and (2) also exist. Here, the isokinetic temperatures for reactions (1), (2), and (3) coincide. At the isokinetic temperature, the rates of replacement of the nitro group and fluorine atom do not depend on the nature of substituent in phenol $[\rho(NO_2) = \rho(F) = 0]$, and the relative mobilities of the nitro group and fluorine atom are similar for all the examined phenols; they are determined by the difference in the free terms of the isokinetic relationships of reactions (1) and (2). Insofar as the isokinetic temperature approaches the range of isoselective temperatures, the rates of replacement of the nitro group and fluorine atom at that temperature are similar (Fig. 1). The isokinetic relationships for reactions (1) and (2) are characterized by similar proportionality coefficients and free terms, which means that reactions (1) and (2) follow a common mechanism; this is supported by fairly small $\Delta\rho$ values calculated for reaction (3) with phenols of both series (Table 3) [31]. The mechanism of reaction (1) and/or (2) changes in going from one phenol series to the other. The character of the $\Delta\Delta H^{\neq}(\Delta\Delta S^{\neq} T)$–p$K_a$ dependence suggests that this change is jumpwise (Fig. 4). The magnitude of distortion of isokinetic relationships in going from one phenol series to the other suggests perturbation of the corresponding reaction mechanism rather than its radical change. Therefore, transition states in the reactions of **I** and **II** with phenols **III–IX** in the presence of K_2CO_3 in DMF are likely to be similar.

In the reaction of **I** and **II** with potassium 5-bromo-3-nitrophenoxide (**IXa**) at 95°C ether **XVI** was formed in 87% yield, whereas an analogous heterogeneous reaction with 5-bromo-3-nitrophenol (**IX**) in the presence of potassium carbonate gave product **XVI** in quantitative yield even at 65°C. In the presence of Cs_2CO_3 as deprotonating agent in reaction (3) with 5-bromo-3-nitrophenol (**IX**) ether **XVI** was obtained in quantitative yield only at 80°C. Thus, there is a relation between the rates of reactions (1) and (2) and nucleophile nature. The relative rate constants of reaction (3) with 4-cresol (**III**) and 5-bromo-3-nitrophenol (**IX**) in the presence of Cs_2CO_3 occupy an intermediate place between those determined under homogeneous (using potassium phenoxides **IIIa** and **IXa**) and heterogeneous conditions
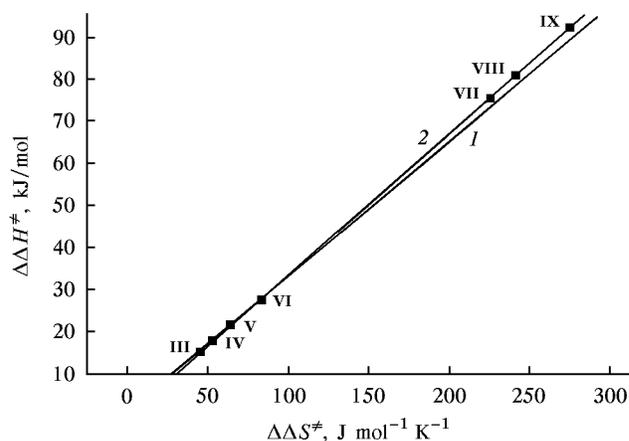
Fig. 3. Plots of $\Delta\Delta H^{\neq}$ versus $\Delta\Delta S^{\neq}$ for reaction (3) with phenols (*1*) **III–VI** and (*2*) **VII–IX** in the presence of potassium carbonate.

(with phenols **III** and **IX** in the presence of K_2CO_3). The way of generation of nucleophilic species insignificantly affects the relative mobility of the nitro group and fluorine atom in reactions with weakly acidic phenols, whereas the same effect in reactions with more acidic phenols is much stronger (Table 1).

It was presumed in [17, 18] that a necessary condition for aromatic nucleophilic substitution by phenols in dipolar aprotic solvents in the presence of potassium carbonate is chemisorption of the reactants on the K_2CO_3 surface. However, addition of 3,5-dinitrobenzotrifluoride (**I**) to a solution, prepared by heating at 70°C potassium carbonate and 3-bromo-5-nitrophenol (**IX**) in DMF under stirring with subsequent removal of the undissolved material, gave 18% of
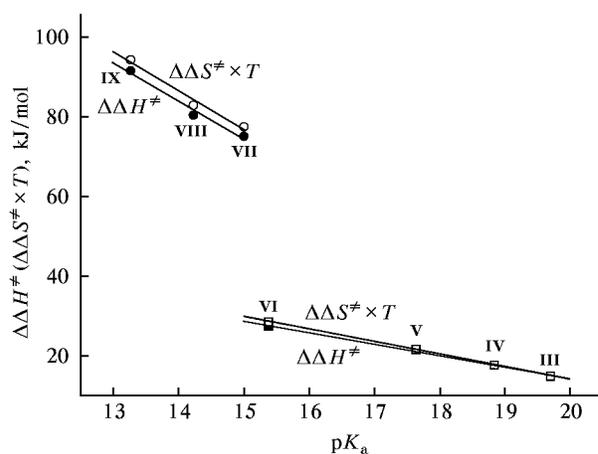
Fig. 4. Plots of $\Delta\Delta H^{\neq}$ (dark circles and squares) and $\Delta\Delta S^{\neq} T$ (light circles and squares) versus pK_a for reaction (3) with phenols **III–VI** and **VII–IX** in the presence of K_2CO_3 at 70°C.

Table 4. Reaction conditions and yields, melting points, and analytical data of compounds **X–XVI** and **XIX**

Initial compounds[a]		Temperature, °C	Product	Yield,[b] %	mp, °C (solvent)	Found M^+	Formula	Calculated M
substrate	phenol							
I	**III**	98	4′-Methyl-3-nitro-	100	51–52	297.06161	$C_{14}H_{10}F_3NO_3$	297.06127
I		70	5-trifluoromethyl-	92	(MeOH)			
II		98	diphenyl ether (**X**)	100				
II		70		91				
I	**IV**	98	3-Nitro-5-trifluoro-	100	21–21.5[c]			
I		70	methyldiphenyl	88				
II		98	ether (**XI**)	100				
II		70		87				
I	**V**	98	4′-Chloro-3-nitro-	100	47–48	317.00697	$C_{13}H_7ClF_3NO_3$	317.00665
I		70	5-trifluoromethyl-	85	(MeOH)			
II		98	diphenyl ether (**XII**)	88				
II		70		84				
I	**VI**	98	3,3′-Dinitro-5-tri-	98	70–70.5	328.03089	$C_{13}H_7F_3N_2O_5$	328.03070
I		70	fluoromethyldi-	65	(EtOH)			
II		98	phenyl ether (**XIII**)	85				
II		70		63				
I	**VII**	98[d]	4′-Acetoxy-3-nitro-5-	99	78–79	325.06161	$C_{15}H_{10}F_3NO_4$	325.06127
I		70	trifluoromethyldi-	52	(EtOH)			
II		98[d]	phenyl ether (**XIV**)	99				
II		70		51				
I	**VIII**	98[d]	3-Nitro-5-trifluoro-	98	63–64	310.0167	$C_{14}H_7F_3N_2O_3$	310.0165
I		70	methyl-4′-cyanodi-	38	(EtOH)			
II		98[d]	phenyl ether (**XV**)	96				
II		70		38				
I	**IX**	98[d]	3′-Bromo-3,5′-dinitro-	98	70–71	405.94231	$C_{13}H_6BrF_3N_2O_5$	405.94126
I		70	5-trifluoromethyldi-	23	(EtOH)			
I		70	phenyl ether (**XVI**)	18				
II		98[d]		95				
II		70		21				
II	**XVIII**	70	3-Nitro-5-trifluoro-	100	50–51	300.54997	$C_{13}H_7F_4NO_3$	300.55013
			methyl-4′-fluorodi-		(MeOH)			
			phenyl ether (**XIX**)					

[a] Molar ratio **I(II)** : ArOH : K_2CO_3 1 : 1 : 1.2.

[b] Method *a*; preparative yield; reaction time 3 h.

[c] Published data [16]: mp 21–21.5°C.

[d] Reaction time 5 h.

diaryl ether **XVI** in 3 h at 70°C. By reaction of **I** with 3-bromo-5-nitrophenol (**IX**) in the presence of K_2CO_3 ether **XVI** was obtained in 23% yield (70°C, 3 h; Table 4). Therefore, the rate of replacement of the nitro group in homogeneous reaction of compound **I** with 3-bromo-5-nitrophenol (**IX**) is close to the rate of the corresponding heterogeneous reactions but is considerably higher than the reaction rate of compound **I** with potassium 3-bromo-5-nitrophenoxide (**IXa**). This means that reaction (1) with 3-bromo-5-nitrophenol (**IX**) in the presence of potassium carbonate cannot be described only as the one occurring on the K_2CO_3 surface and that it also differs from the reaction of **I** with 3-bromo-5-nitrophenoxide ion (**IXa**).

4-Cyanophenol is known to smoothly react with nitrobenzene derivatives in DMSO in the presence of KF to afford products of replacement of the nitro group by 4-cyanophenoxy group. Here, the nucleo-

Table 5. ^{19}F NMR spectra of the reaction mixture obtained from 3-fluoro-5-nitrobenzotrifluoride (**II**), 4-fluorophenol (**XVIII**), and K_2CO_3 in DMF

Sample no.	Temperature, °C	Signal intensity ratio[a] (δ_F, ppm)			
		CF$_3$	3-F	4-F	4′-F
1[b]	25	3.0 (101.46)	1.0 (56.92)	1.0 (36.28)	0 (45.91)
2	25	3.0 (101.46)	1.0 (56.92)	1.0 (34.97)	0 (45.91)
3[c]	70	3.0 (101.46)	0.9 (56.92)	0.9 (34.27)	0.1 (45.91)
4	70	3.0 (101.36)	0.7 (56.92)	0.7 (34.05)	0.3 (45.91)
5	70	3.0 (101.33)	0.5 (56.92)	0.5 (33.96)	0.5 (45.91)

[a] 3-F denotes the fluorine atom in position *3* of compound **II**; 4-F stands for the 4-fluorine atom in 4-fluorophenol (**XVIII**); 4′-F is the fluorine atom in position *4′* of ether **XIX**; and CF$_3$ corresponds to the overall signal of the CF$_3$ group in compounds **II** and **XIX**.
[b] Sample no. 1 was withdrawn immediately after mixing the reactants, and the other samples were withdrawn each 20 min.
[c] After withdrawal of sample no. 3, the mixture was heated to 70°C.

philic species is a complex of 4-cyanophenol with KF, which was characterized by IR spectroscopy [32]. Comparison of the IR spectrum of a sample, prepared by keeping potassium carbonate with 4-cyanophenol (**VIII**) in DMF at 70°C and subsequent filtration, with the IR spectra of solutions of 4-cyanophenol and potassium 4-cyanophenoxide in DMF suggests that such a complex is actually formed. Stretching vibrations of the cyano group in 4-cyanophenol and 4-cyanophenoxide ion appear at 2222 and 2185 cm^{-1}, respectively. In the spectrum of the assumed complex two bands at 2206 and 2189 cm^{-1} were present, while absorption typical of OH stretching vibrations in 4-cyanophenol (3077 cm^{-1}) was absent. The greater shift of the ν(CN) band in going from 4-cyanophenol to its complex with K_2CO_3, as compared to the complex with KF, indicates greater charge delocalization in the former complex [32].

The ^{19}F NMR spectrum of a solution, prepared by keeping potassium carbonate and 4-fluorophenol (**XVIII**) in DMF at 70°C with subsequent filtration from undissolved material, contains a singlet at δ_F 33.36 ppm (t.t). This value is intermediate between the ^{19}F chemical shifts of 4-fluorophenol and potassium 4-fluorophenoxide in DMF, δ_F 36.28 (t.t) and 31.64 ppm (br.s), respectively. Using ^{19}F NMR spectroscopy, it was also shown that during the reaction of 3-fluoro-5-nitrobenzotrifluoride (**II**) with 4-fluorophenol in the presence of potassium carbonate signals corresponding to compound **II** and 4-fluorophenol disappear at equal rates coinciding with the rate of appearance of the signal at δ_F 45.34 ppm which belongs to 4′-F in diaryl ether **XIX**; here, the intensity of the CF$_3$ signal remains unchanged (Table 5). These data indicate that the reaction proceed mainly in solution

rather than on the K_2CO_3 surface. The upfield shift of the signal from 4-fluorophenol at room temperature suggests higher rate of complex formation, as compared to the rate of substitution (Table 5).

Taking into account that potassium carbonate is very poorly soluble in DMF [21], the relatively high rate of formation of the corresponding complex may be explained by processes occurring on the K_2CO_3 surface. Probably, initially chemisorbed phenol molecule irreversibly leaves the K_2CO_3 surface together with potassium carbonate molecule, i.e., as a complex with the deprotonating agent [33]. This assumption can explain a satisfactory correlation between the rate of replacement of the nitro group in 4-nitrophthalonitrile by phenols in the presence of alkali metal carbonates M_2CO_3 and the energy of their crystal lattice [21]. Obviously, coordination of phenol at the K_2CO_3 surface should affect mutual orientation of the phenol and potassium carbonate molecules in the corresponding complex. Irreversible desorption is typical of strong chemisorption bonds; therefore, the complex thus formed should be fairly stable. Dorogov *et al.* [18] presumed formation of a cyclic adsorption complex via phenol coordination at an active part of the M_2CO_3 surface. An analogous cyclic structure may be assigned to the complex [ArOH·K$_2$CO$_3$], as well as to [4-CNC$_6$H$_4$OH·KF] [32].

Assuming a common mechanism of reactions (1) and (2), the reactions of compounds **I** and **II** with phenols **III**–**IX** and **XVIII** in the presence of K_2CO_3 in DMF can be considered to occur as replacement of the nitro group and fluorine atom by the action of the corresponding phenol–potassium carbonate complex [ArOH·K$_2$CO$_3$] in solution. Then, chelate structures **A** and **B** may be proposed for transition states (TS)

at the stage of formation of σ-complex in reactions (2) and (1), respectively:

[ArOH·K₂CO₃]
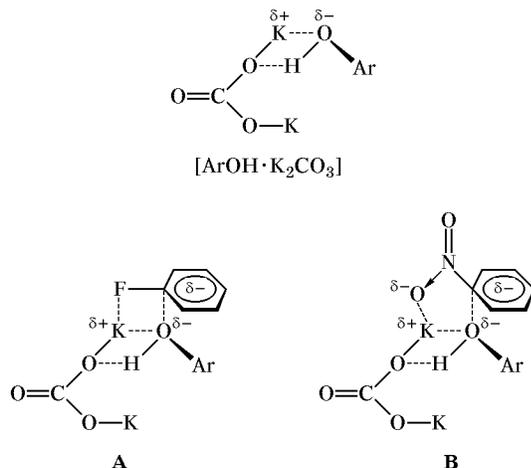
On the basis of the relation between the stability of coordination compounds and their structure, transition states **A** and **B** are expected to be stabilized to a sufficient extent, structure **B** being stabilized better than **A**. Formation of a chelate ring is known to increase the stability of coordination compounds, and increase in the number of chelate rings enhances this tendency [34]. Therefore, the transition states can be stabilized additionally via formation of chelate-like cyclic structures **A** and **B**. It should be noted that coordination compounds with small chelate rings are more stable than analogous carbocycles, since the atoms and bonds in the former are not similar [35]. Five-membered chelate rings are more stable than four-membered; therefore, structure **B** should be more stable than **A** [34]. Presumably, the reactions of **I** and **II** with the complexes [ArOH·K₂CO₃] follow a coordination catalysis mechanism, according to which nucleophilic attack on the complex is possible due to additional assistance by complex formation preceding or occurring simultaneously with the rate-determining stage (formation of σ-complex [36]). Stepwise mechanism includes intramolecular nucleophilic attack which is more favorable than inter-molecular [37]. In the case of a concerted mechanism, the corresponding transition state is stabilized by considerable electron density delocalization via electron transfer [38]. In both cases, complex formation not only creates favorable steric conditions for formation of transition states but also enhances the reactivity of the components [38].

Reactions following a coordination catalysis mechanism with synchronous formation of TS are characterized by very low energies of activation and similar but high entropies of activation [39]. Analysis of the $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values for reaction (3) with strongly acidic phenols **VII–IX** from the viewpoint of the possibility for synchronous mechanism shows that the stage of formation of σ-complex in reaction (2) requires much lower enthalpy of activation and a strictly definite mutual orientation of the reactants, as compared to the corresponding stage of reaction (1). In going to reactions (3) with weakly acidic phenols **III–VI**, the $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values suggest closer activation parameters for the formation of σ-complex in reactions (1) and (2) as the acidity of phenol decreases. Obviously, a synchronous mechanism is hardly probable for the reactions of **I** and **II** with the [ArOH·K₂CO₃] complexes.

It should be specially emphasized that in stepwise bimolecular reactions the efficiency of coordination catalysis is determined mainly by the possibility for formation of an intermediate complex with rigorous mutual reactant orientation. This factor favors the reactions via increased activation entropy [40].

The apparent rate constants of reactions (1) and (2) with stepwise formation of transition states **A** and **B** include not only the rate constant of nucleophilic attack but also the corresponding complex formation constant. Therefore, the parameters $\Delta\Delta H^{\neq}$, $\Delta\Delta S^{\neq}$, $\Delta\rho$, and $\Delta\beta_{Nuc}$ are composite quantities describing the overall process (complex formation stage and nucleophilic attack). In this case, the fulfilment of the Brønsted and Hammett dependences for reactions (1) and (2) implies that they are also valid for each stage taken separately.

Structures **A** and **B** suggest that in the course of nucleophilic attack the dative bond between the phenolic oxygen atom and potassium cation becomes weaker while the bond between K⁺ and fluorine atom (in compound **II**) or oxygen atom of the nitro group in **I** strengthens. It is known that complex formation exerts some effect on bonds neighboring to the dative ones [40]; therefore, the positive charge on the electrophilic center in **II** may increase due to cyclic charge transfer. This should reduce the enthalpy of formation of σ-complex, i.e., the $\Delta H^{\neq}(F)$ value. Simultaneously, the entropy of TS decreases, and $\Delta S^{\neq}(F)$ increases. A combination of these factors is equivalent to introduction of an additional electron-acceptor substituent into the corresponding phenol and shift of TS along the reaction coordinate toward later states. Clearly, a necessary condition is sufficiently late TS and fairly high nucleophilicity of the reagent. Thus, in terms of the proposed scheme we should expect (a) similar transition states in reactions (1) and (2) for each phenol and (b) jumpwise perturbation

of the mechanism of reaction (2) (due to cyclic charge transfer) in going to more acidic phenols. These expectations are well consistent with the results of analysis of correlations obtained for competing reactions (3).

The following conclusions can be drawn: (1) Substitution of the nitro group in compound **I** and of the fluorine atom in **II** by the action of [ArOH·K_2CO_3] in the examined temperature range includes initial complex formation stage and subsequent intramolecular nucleophilic attack; (2) In reaction (2) additional stabilization via cyclic charge transfer is possible; (3) The higher reactivity of the nitro group in **I**, as compared to the fluorine atom in **II**, is explained in terms of the entropy control whose contribution increases as the nucleophilicity of the reagent rises (Fig. 4); (4) The effect of the substituent in phenol on the relative reactivity of the nitro group and fluorine atom is determined by the overall sensitivity of the nucleophilic attack and complex formation stages to that factor. Taking into account that complexing power of eight-electron cations increases as their radius decreases [41], the proposed mechanism is less probable in the presence of cesium carbonate.

We also tried to reveal the effect of K_2CO_3 on the reactivity of nitrite and fluoride ions released in competing reactions (3). For this purpose we examined reactions of compounds **I** and **II** with KNO_2 and KF in the presence and in the absence of potassium carbonate (Table 6). The results showed that K_2CO_3 clearly affects only the rate of reactions of **I** and **II** with ambident nitrite ion as O-nucleophile. The observed effect may be explained by preliminary coordination of nitrite ion to potassium carbonate in a way similar to coordination of phenol in the complex [ArOH·K_2CO_3] and formation of a cyclic transition state.

Thus *meta,meta*-activated arenes containing highly nucleofugic substituents such as nitro group and fluorine atom react with phenols in the presence of potassium carbonate in a stepwise mode involving formation of a cyclic transition state with participation of K_2CO_3 at the stage of nucleophilic attack. Obviously, an analogous mechanism could be expected not only for neutral nucleophiles (such as phenols, alcohols, thiols, and amines) but also for charged species (such as nitrite and azide ions).

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra of 10% solutions in CCl_4 were recorded on a Bruker WP 200SY spectrometer using HMDS and C_6F_6 as internal references.

Table 6. Product ratios in the reactions of compounds **I** and **II** with KNO_2 and KF in the presence and in the absence of K_2CO_3 (DMF, 95°C, 3 h)[a]

Comp. no.	KNO_2	KF	K_2CO_3	Composition of the reaction mixture,[b] mmol		
				I	**II**	**XVII**
I	+	–	+	0.450	–	0.050
I	–	+	+	0.485	0.010	0.005
I	+	–	–	0.500	–	–
I	–	+	–	0.495	0.005	–
II	+	–	+	0.010	0.480	0.010
II	+	–	–	0.040	0.460	–

[a] Initial reactant ratio, mol: **I** (or **II**):KNO_2 (or KF):K_2CO_3, 5:1:1.2.
[b] GLC data.

The IR spectra of 2% solutions in DMF and CCl_4 were obtained on a Specord M-80 instrument. GLC analysis of the reaction mixtures was performed on an LKhM-72 chromatograph (heat conductivity detector; 4000 × 4-mm column packed with 15% of SKTFT-803 on Chromaton-W; carrier gas helium; linear oven temperature programming from 70 to 270°C at a rate of 10 deg/min). The components were quantitated by the absolute calibration technique using preliminarily plotted calibration curves and were identified by addition of authentic samples. The mass spectra (70 eV) were run on a Finnigan MAT-8200 spectrometer (ion source temperature 100–220°C). Silufol UV-254 plates were used for thin-layer chromatography (eluent CCl_4).

Commercial dimethylformamide was dried over 4-Å molecular sieves and distilled under reduced pressure over CaH_2. Commercial phenols **III**–**IX** and **XVIII** were purified by standard procedures. Commercial KNO_2, KF, and K_2CO_3 were dehydrated by calcination and were then ground. 3,5-Dinitrobenzotrifluoride (**I**) and 3-fluoro-5-nitrobenzotrifluoride (**II**) were synthesized as described in [16], mp 47–48°C (**I**) and bp 67–68°C (4 mm; **II**); their constants coincided with published date. 3-Bromo-5-nitrophenol (**IX**) was prepared by demethylation of 3-bromo-5-nitroanisole by the action of HBr [42], mp 145°C [43]; 3-bromo-5-nitroanisole was in turn synthesized by replacement of one nitro group in 1-bromo-3,5-dinitrobenzene by methoxy [2]. Potassium phenoxides **IIIa**, **VIIIa**, **IXa**, and **XVIIIa** were synthesized by the procedure reported in [44].

Table 7. ^{1}H and ^{19}F NMR and IR spectra of compounds **X**, **XII–XVI**, and **XIX**[a]

Comp. no.	^{1}H NMR spectrum, δ, ppm (J, Hz)	^{19}F NMR spectrum, δ_F, ppm	IR spectrum,[b] ν, cm^{-1}
X	2.40 s (3H, CH$_3$), 6.88–6.98 d.m (2H, 2′-H, 6′-H, 8.0), 7.17–7.27 d.m (2H, 3′-H, 5′-H, 8.0), 7.48 m (1H, 6-H), 7.84 m (1H, 2-H), 8.08 m (1H, 4-H)	98.41 s (CF$_3$)	1545 s, 1350 s (NO$_2$); 1230 s, 1086 m (C−O−C); 655 m (C−F)
XII	6.97–7.10 d.m (2H, 2′-H, 6′-H, 9.0), 7.30–7.43 d.m (2H, 3′-H, 5′-H, 9.0), 7.43–7.48 m (1H, 6-H), 7.85–7.90 m (1H, 2-H), 8.16 m (1H, 4-H)	98.41 s (CF$_3$)	1545 s, 1350 s (NO$_2$); 1232 s, 1087 m (C−O−C); 687 m (C−F); 681 m (C−Cl)
XIII	7.32–7.42 d.m (1H, 6′-H, 7.0), 7.58 m (1H, 6-H), 7.56–7.70 m (1H, 5′-H), 7.88–7.94 m (1H, 2′-H), 7.94–7.99 m (1H, 2-H), 8.06–8.16 d.m (1H, 4′-H, 9.2), 8.26 m (1H, 4-H)	98.43 s (CF$_3$)	1537 s, 1344 s (NO$_2$); 1231 s, 1087 m (C−O−C); 697 m (C−F)
XIV	1.23 s (3H, COCH$_3$), 7.06–7.14 d.m (2H, 2′-H, 6′-H, 9.0), 7.55 m (1H, 6-H), 7.95–8.09 m (3H, 2-H, 3′-H, 5′-H), 8.22 m (1H, 4-H)	98.41 s (CF$_3$)	1706 s (C=O); 1504 s, 1345 s (NO$_2$); 1233 s, 1085 m (C−O−C), 695 m (C−F)
XV	7.10–7.15 d.m (2H, 2′-H, 6′-H, 8.5), 7.58 m (1H, 6-H), 7.72–7.75 d.m (2H, 3′-H, 5′-H, 8.5), 7.99 m (1H, 2-H), 8.27 m (1H, 4-H)	98.38 s (CF$_3$)	2213 s (CN); 1500 s, 1348 s (NO$_2$); 1238 s, 1087 m (C−O−C); 685 m (C−F)
XVI	7.50–7.51 m (1H, 5′-H), 7.59 m (1H, 6-H), 7.80–7.81 m (1H, 4′-H), 8.00 m (1H, 2-H), 8.25–8.26 m (1H, 2′-H), 8.32 m (1H, 4-H)	98.41 s (CF$_3$)	1540 s, 1342 s (NO$_2$); 1231 s, 1085 m (C−O−C); 692 m (C−F); 683 m (C−Br)
XIX	6.95–7.18 m (4H, 2′-H, 3′-H, 5′-H, 6′-H), 7.49 m (1H, 6-H), 7.87 m (1H, 2-H), 8.15 m (1H, 4-H)	98.40 s (CF$_3$), 45.34 m (4′-F)	1546 s, 1353 s (NO$_2$); 1232 s, 1089 m (C−O−C); 685 m (C−F)

[a] The spectral parameters of compounds **XI** and **XVII** were reported in [16].
[b] In CCl$_4$.

Reaction of compounds I and II with phenols III–IX in the presence of potassium carbonate in DMF (*Method a*) (Table 4). To a 10% solution of compound **I** or **II** in DMF we added phenol **III–IX** or **XVIII**, and freshly calcined K$_2$CO$_3$, and the mixture was stirred on heating. The progress of the reaction was monitored by TLC. The mixture was cooled, the precipitate was filtered off and washed with methylene chloride on a filter, and the filtrate was evaporated. The products (Table 7) were isolated by chromatography on a 35 × 150-mm column charged with Al$_2$O$_3$ of activity grade II (40/250 μm) using CCl$_4$ as eluent and were additionally purified by recrystallization.

Reaction of compound I with 3-bromo-5-nitrophenol IX in the presence of K$_2$CO$_3$ in DMF (*Method b*) (Table 4). Potassium carbonate was added to a 10% solution of 3-bromo-5-nitrophenol in DMF, the mixture was stirred for 3 h at 70°C and cooled, and the precipitate was filtered off. Compound **I** was added to the filtrate, and the mixture was stirred for 3 h at 70°C, cooled, and analyzed by GLC.

Determination of the relative reactivity of compounds I and II toward phenols III–IX in the presence of K$_2$CO$_3$ and Cs$_2$CO$_3$. Phenol **III–IX** and freshly calcined K$_2$CO$_3$ or Cs$_2$CO$_3$ were added to a 10% solution of compounds **I** and **II** in DMF, and the mixture was stirred on heating. It was then cooled, and the precipitate was filtered off and washed with methylene chloride on a filter. The solvent was distilled off from the filtrate, and the residue was analyzed by GLC. The conditions and results of typical experiments are available from the authors.

Determination of the relative reactivity of compounds I and II toward potassium 4-methylphenoxide (IIIa) and potassium 3-bromo-5-nitrophenoxide (IXa) in DMF. Potassium phenoxide **IIIa** or **IXa** was added to a 10% solution of compounds **I** and **II** in DMF, and the mixture was stirred on heating. It was then cooled, the precipitate was filtered off and washed with methylene chloride on a filter, the filtrate was evaporated, and the residue was analyzed by GLC. The conditions and results are available from the authors.

Reactions of 4-cyanophenol (VIII) and 4-fluoro-phenol (XVIII) with K$_2$CO$_3$ in DMF. Potassium carbonate, 0.083 g (0.6 mmol), was added to a 2% solution of 0.06 g (0.5 mmol) of phenol **VIII** or **XVIII** in DMF, and the mixture was stirred for 3 h at 70°C. The resulting suspension was cooled, and the precipitate was filtered off. The filtrate was examined by ^{19}F NMR spectroscopy (for 4-fluorophenol) or IR spectroscopy (for 4-cyanophenol); the spectral parameters were then compared with those of the corresponding phenols and their potassium salts.

^{19}F NMR study of the reaction of compound II with 4-fluorophenol (XVIII) in DMF in the presence of K$_2$CO$_3$. Phenol **XVIII**, 0.123 g (1.1 mmol), and freshly calcined potassium carbonate, 0.183 g (1.3 mmol), were added to a 10% solution of 0.152 g (1.1 mmol) of compound **II** in DMF, and the mixture was stirred. Samples were withdrawn at specified time intervals and were analyzed by ^{19}F NMR spectroscopy (see Table 5).

Reactions of compounds I and II with KNO$_2$ and KF in DMF in the presence and in the absence of potassium carbonate. Freshly calcined potassium nitrite or potassium fluoride and, if necessary, potassium carbonate were added to a 10% solution of compound **I** or **II** (0.5 mmol) in DMF, and the mixture was stirred at 95°C. It was then cooled, the precipitate was filtered off and washed with methylene chloride on a filter, the filtrate was evaporated, and the residue was analyzed by GLC. The conditions and results of these experiments are summarized in Table 6.

REFERENCES

1. Idoux, J.P., Madenwald, M.L., Garcia, B.S., and Chu, D.-L., *J. Org. Chem.,* 1985, vol. 50, no. 11, pp. 1876–1878.

2. Effenberger, F. and Streicher, W., *Chem. Ber.,* 1991, vol. 124, no. 1, pp. 163–173.

3. Terrier, F., *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group,* Weinheim: VCH, Inc., 1991, part 1, pp. 21–29.

4. Terrier, F., *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group,* Weinheim: VCH, 1991, part 2, pp. 158–169.

5. Effenberger, F. and Streicher, W., *Chem. Ber.,* 1991, vol. 124, no. 1, pp. 157–162; Maggini, M., Pasudetti, M., Gonsales-Trueba, G., Prato, M., Quintilly, U., and Scorrano, G., *J. Org. Chem.,* 1991, vol. 56, no. 22, pp. 6406–6411.

6. Bartoli, G., Latrofa, A., Naso, F., and Todesco, P.E., *J. Chem. Soc., Perkin Trans. 1,* 1972, no. 21, p. 2671.

7. Gitis, S.S. and L'vovich, I.G., *Zh. Obshch. Khim.,* 1964, vol. 34, no. 7, pp. 2250–2254.

8. Kornblum, N., Cheng, L., Kerber, R.C., Kestner, M.M., Newton, B.N., Pinnick, N.W., Smith, R.G., and Wade, P.A., *J. Org. Chem.,* 1976, vol. 41, no. 9, pp. 1560–1564.

9. Plakhtinskii, V.V., Dorogov, M.V., Khokhlov, A.L., and Krasovskaya, G.G., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1996, vol. 39, no. 3, pp. 3–7.

10. Buncell, E. and Manderville, R.A., *J. Phys. Org. Chem.,* 1993, vol. 6, no. 1, pp. 71–82.

11. Terrier, F., *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group,* Weinheim: VCH, 1991, part. 1, pp. 85–94.

12. Stahly, G.P., *J. Org. Chem.,* 1985, vol. 50, no. 17, pp. 3091–3094.

13. Shevelev, S.A., Dutov, M.D., Vatsadze, I.A., Serushkina, O.V., Rusanov, A.L., and Andrievskii, A.M., *Mendeleev Commun.,* 1995, no. 4, pp. 157–158; Shevelev, S.A., Dutov, M.D., and Serushkina, O.V., *Izv. Akad. Nauk, Ser. Khim.,* 1995, no. 12, pp. 2528–2529.

14. JPN Patent no. 07-118 212, 1995; *Chem. Abstr.,* 1995, vol. 123, no. 82 943; EU Patent no. 193 358, 1986; *Chem. Abstr.,* 1986, vol. 105, no. 226 036 q.

15. Khalfina, I.A. and Vlasov, V.M., *Russ. J. Org. Chem.,* 1997, vol. 33, no. 5, pp. 665–670.

16. Khalfina, I.A., Rogozhnikova, O.Yu., and Vlasov, V.M., *Russ. J. Org. Chem.,* 1996, vol. 32, no. 9, pp. 1328–1331.

17. Kaninskii, P.S., Plakhtinskii, V.V., Mironov, G.S., and Ryabukhina, N.S., *Osnov. Org. Sintez Neftekhim.,* 1986, no. 22, pp. 71–76.

18. Dorogov, M.V., Yasinskii, O.A., Plakhtinskii, V.V., and Pliss, E.M., *Russ. J. Org. Chem.,* 1999, vol. 35, no. 8, pp. 1171–1175.

19. Kiperman, S.L., *Osnovy khimicheskoi kinetiki v geterogennom katalize* (Principles of Chemical Kinetics in Heterogeneous Catalysis), Moscow: Khimiya, 1979, pp. 204–218.

20. US Patent no. 4 990 670, 1991; *Chem. Abstr.,* 1991, vol. 114, no. 206 762 f.

21. Kaninskii, P.S., Abramov, I.G., Yasinskii, O.A., Mironov, G.S., and Plakhtinskii, V.V., *Zh. Org. Khim.,* 1992, vol. 28, no. 6, pp. 1232–1235.

22. Tabatskaya, A.A., Vyalkov, A.I., Morozov, S.V., and Vlasov, V.M., *Russ. J. Org. Chem.,* 1998, vol. 34, no. 11, pp. 1654–1659.

23. Gordon, A.J. and Ford, R.A., *The Chemist's Companion,* New York: Wiley, 1972. Translated under the title *Sputnik khimika,* Moscow: Mir, 1976, p. 159.

24. Ritchie, C.D. and Sager, W.F., *Progress in Physical Organic Chemistry,* Cohen, S.G., Streitwieser, A., Jr., and Taft, R.W., Eds., New York: Intersci., 1963, vols. 1, 2. Translated under the title *Sovremennye problemy fizicheskoi organicheskoi khimii*, Moscow: Mir, 1967, pp. 498–555.

25. Hansch, C., Leo, A., and Taft, R.W., *Chem. Rev.,* 1991, vol. 91, no. 2, pp. 165–195.

26. Bordwell, F.G. and Cheng, J.-P., *J. Am. Chem. Soc.,* 1991, vol. 113, no. 5, pp. 1736–1743.

27. Maran, F., Celadon, D., Severin, M.G., and Vianello, E., *J. Am. Chem. Soc.,* 1991, vol. 113, no. 24, pp. 9320–9329.

28. Hammett, L., *Physical Organic Chemistry*, New York: McGraw–Hill, 1970, 2nd ed. Translated under the title *Osnovy fizicheskoi organicheskoi khimii*, Moscow: Mir, 1972, pp. 504–525; Pal'm, V.A., *Osnovy kolichestvennoi teorii organicheskikh reaktsii* (Principles of the Quantitative Theory of Organic Reactions), Leningrad: Khimiya, 1977, pp. 260–276.

29. Hoz, S., *Acc. Chem. Res.,* 1993, vol. 26, no. 2, pp. 69–74.

30. Buncel, E. and Wilson, H., *J. Chem. Educ.,* 1987, vol. 64, no. 6, pp. 475–480; Exner, O., *J. Chem. Soc., Perkin Trans. 2,* 1993, no. 5, pp. 973–976.

31. Zhdanov, Yu.A. and Minkin, V.I., *Korrelyatsionnyi analiz v organicheskoi khimii* (Correlation Analysis in Organic Chemistry), Rostov-on-Don: Rostov. Gos. Univ., 1966, pp. 41–55.

32. Clark, J.H. and Owen, N.D.S., *Tetrahedron Lett.,* 1987, vol. 28, no. 31, pp. 3627–3630.

33. Boreskov, G.K., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Nauka, 1986, p. 99.

34. *Theoretical Inorganic Chemistry,* Day, M.C., Jr. and Selbin, J., Eds., New York: Reinhold, 1969, 2nd ed. Translated under the title *Teoreticheskaya neorganicheskaya khimiya,* Moscow: Khimiya, 1976, p. 454.

35. Perry, R., *The Chemistry of the Coordination Compounds,* Bailar, J.C. and Busch, D.H., Eds., New York: Reinhold, 1956. Translated under the title *Khimiya koordinatsionnykh soedinenii,* Moscow: Inostrannaya Literatura, 1960, chap. 5, pp. 186–190.

36. Litvinenko, L.M. and Oleinik, N.M., *Organicheskie katalizatory i gomogennyi kataliz* (Organic Catalysts and Homogeneous Catalysis), Kiev: Naukova Dumka, 1981, pp. 174–230.

37. Terrier, F., *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group,* Weinheim: VCH, 1991, chap. 2, pp. 128–131.

38. Becker, H., *Einführung in die Elektronentheorie organisch–chemischer Reaktionen,* Berlin: Wissenschaften, 1974, 3rd ed. Translated under the title *Vvedenie v elektronnuyu teoriyu organicheskikh reaktsii*, Moscow: Mir, 1977, p. 342.

39. Savelova, V.A. and Oleinik, N.M., *Mekhanizmy deistviya organicheskikh katalizatorov. Bifunktsional'nyi i vnutrimolekulyarnyi kataliz* (Mechanisms of Action of Organic Catalysts. Difunctional and Intramolecular Catalysis), Kiev: Naukova Dumka, 1990, pp. 78–79.

40. Siling, M.I. and Gel'bshtein, A.I., *Usp. Khim.,* 1969, vol. 38, no. 3, pp. 479–500.

41. Skorik, N.A. and Kumok, V.N., *Khimiya koordinatsionnykh soedinenii* (Chemistry of Coordination Compounds), Moscow: Vysshaya Shkola, 1975, p. 62.

42. *Weygand–Hilgetag organisch-chemische Experimentierkunst,* Hilgetag, G. and Martini, A., Eds., Leipzig: Johann Ambrosius Barth, 1964, 3rd ed. Translated under the title *Metody eksperimenta v organicheskoi khimii,* Moscow: Khimiya, 1968, p. 361.

43. *Beilsteins Handbuch der organischen Chemie,* EII, vol. 6, p. 233.

44. Kornblum, N. and Lurie, A.P., *J. Am. Chem. Soc.,* 1959, vol. 81, no. 8, p. 2705.

45. Williams, F.J. and Donahue, P.E., *J. Org. Chem.,* 1977, vol. 42, no. 21, pp. 3414–3418.