===

Nucleophilic Reactivity. Kinetics of Reactions between Diarylamines N-Anions and Hexafluorobenzene or Pentafluoropyridine in Dimethyl Sulfoxide[*]

I. A. Os'kina and V. M. Vlasov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Abstract—Rate constants of reactions between sodium salts of diarylamines N-anions and hexafluorobenzene and pentafluoropyridine in DMSO at 25°C were determined. The Bronsted factors for substrates under consideration are 0.14 and 0.34 respectively. These data evidence a considerable effect of substrate electrophilicity on the reactivity of diarylamines N-anions in the S_NAr reactions. Deviations of the Bronsted plot from linearity for the reactions of hexafluorobenzene with aryl-and diarylamines N-anions may be due to the difference in internal barriers of these reactions.

Linear correlations for free energies of various kinds, e.g. equations of Swaine-Scott, Edwards, Brønsted or Ritchi are important for the study of nucleophilic reactivity [1, 2]. The Brønsted equation turned out especially useful for description of S_N2-reactions [3, 4]. Yet the range of Brønsted factor (β_{Nuc} ~0.2–0.5 [3]) for S_N2-reactions is not characteristic of S_NAr-reactions where the value β_{Nuc} varies in wider limits (0.2–0.9) [5, 6]. One cause of β_{Nuc} variation in the S_NAr-reactions is the considerable influence of the steric effects in the nucleophile; their increase reduces the β_{Nuc} factor value [6]. Another reason for variations in the β_{Nuc} value is the electrophilicity of a substrate although this cause of variations in the Brønsted factor is less understood (cf. [5]).Thus the β_{Nuc} factor for the reaction of 4-nitrofluorobenzene with a series of arylfluorenyl anions is by 0.11–0.15 greater than for reaction of the less electrophilic 4-cyanofluorobenzene with a series of 9-methylfluorenyl anions in DMSO [5]. Similarly for the reaction of amines with picrylchloride the β_{Nuc} value is by 0.12 greater than for the reaction of amines with 2,4-dinitrochlorobenzene in water medium [7]. Slight variations in the β_{Nuc} factor are also observed for reactions of O- and S-anions with various arenes. For the reaction of substituted phenolates with 2-nitro-4-R-chlorobenzenes in 80% aqueous dioxane at 65°C the β_{Nuc} factor is 0.76 and

0.81 at R = Cl and R = NO$_2$ respectively although the rates differ by 4 orders of magnitude [8]. For the same reaction at R = CHO in EtOH at 40°C the β_{Nuc} value is smaller, 0.56 [9], and at R = NO$_2$ in MeOH at 25.9°C and 50°C the value of the factor β_{Nuc} increases to 0.91 [10, 11]. However for the reactions of picrylchloride with substituted phenolates in 75% aqueous ethanol at 30°C the β_{Nuc} value equals to 0.83 [12] although the reaction velocity increases by four orders of magnitude as compared with the preceding reaction of 2,4-dinitrochlorobenzene. The Brønsted plots for reactions of 4-nitro- and 2,4-dinitrochlorobenzenes with substituted thiophene oxides in methanol and 95% aqueous ethanol have slopes equal to 0.48 and 0.65 respectively whereas the reactivity of both substrates differs by 6 orders of magnitude [13].

The above values of β_{Nuc} for S_NAr reactions of C-, N-, O-, and S-nucleophiles were obtained under different reaction conditions. This fact hampers the analysis of the effect of substrate electrophilicity on the β_{Nuc} value. We formerly reported on reactivity of arylamines N-anions toward 4-nitrofluorobenzene and hexafluorobenzene in DMSO at 25°C. The reaction rates with hexafluorobenzene were higher [6, 14]. Yet the published data on reactivity of 4-nitrofluorobenzene and hexafluorobenzene toward methylate ion [15, 16], thiophenolate ion [15, 17], azide ion [15, 18], and piperidine [18, 19] demonstrated that the rate constant of reaction of the above ions with 4-nitrofluorobenzene was about one order of magnitude greater than that with hexafluorobenzene.

Still greater difference in reactivity toward, e.g., methylate ion is observed in reaction with hexafluorobenzene and pentafluoropyridine: it reaches about 7 orders of magnitude [20]. Therefore in this study we undertook an investigation of reactivity of a series of diarylamines N-anions with these substrates significantly different in electrophilicity.

$$ArNHAr' \xrightarrow[\substack{DMSO, \\ 25°C}]{NaH} \begin{matrix} Na \\ ArNAr' \\ \mathbf{Ia-VIIa} \end{matrix}$$

(1)
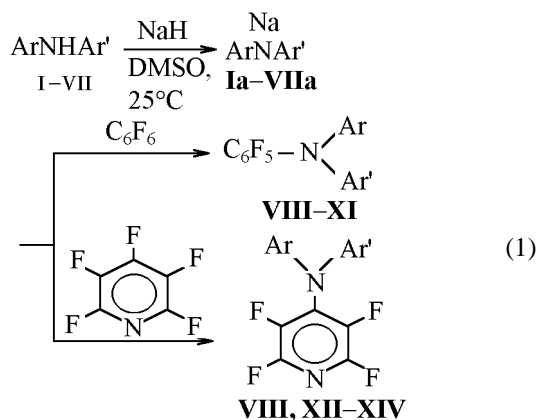
Ar = C_6F_5, Ar' = 4-C_5F_4N (**I, Ia, VIII, XII**); Ar = C_6F_5, Ar' = 4-ClC_6F_4 (**II, IIa, IX**); Ar = Ar' = C_6F_5 (**III, IIIa, VIII**); Ar = C_6F_5, Ar' = 4-$CH_3C_6F_4$ (**IV, IVa, XIII**); Ar = Ph, Ar' = 4-CNC_6F_4 (**V, Va, X**); Ar = Ph, Ar' = 4-C_5F_4N (**VI, VIa, XIV**); Ar = Ph, Ar' = 4-$NO_2C_6H_4$ (**VII, VIIa, XI**).

The choice of N-anions of diarylamines **Ia–VIIa** is justified by the fact that this anion series includes sufficiently large range of basicities (Table 1) for revealing the causes of variations in the factor β_{Nuc} for S_NAr reactions. Although N-anions of diarylamines **I–IV** unlike those of diarylamines **V–VII** contain at the reaction center additional *ortho*-fluorines the latter would not contribute any sterical effect into the nucleophilicity of the N-anions **Ia–IVa** originating from diarylamines since the sterical constants of the phenyl and *ortho*-fluorophenyl groups have close values (R_s 0.145 and 0.152 respectively [21]). Besides previously was demonstrated that in reaction with 4-nitrofluorobenzene the Brønsted correlation between nucleophilicity and basicity is valid for N-anions of both fluorinated and unfluorinated aryl- and diarylamines [6]. This fact evidences that the steric effect of ortho-fluorine atoms in the benzene ring is insignificant. As seen from the structure of N-anions **Ia–VIIa** [equation (1)], nearly all of them contain electron-acceptor groups in the resonance positions of the benzene ring. The presence of these groups may affect the relation between nucleophilicity

Table 1. Second order rate constants (k) for reactions of diarylamines N-anions $N^-Ar'Na^+$ (**Ia–VIIa**) with hexafluorobenzene and pentafluoropyridine in DMSO at 25°C, and acidity of compounds ArNHAr' (**I–VII**) in DMSO (pK), 25°C

Compd. no. ArNHAr'	pK [a]	Compd. no. ArN$^-$Ar'Na$^+$	$k \times 10^3$, 1 mol^{-1} s^{-1} [b]	
			C_6F_6	C_5F_5N
I	9.4	**Ia**	0.212 ± 0.070 (3)	2.31 ± 0.40 (3)
II	12.0	**IIa**	0.373 ± 0.078 (4)	–
III	12.6	**IIIa**	–	31.1 ± 1.4 (7)
IV	13.3	**IVa**	–	84.1 ± 12.4 (5)
V	14.7	**Va**	1.53 ± 0.43 (4)	–
VI	15.1	**VIa**	–	169 ± 23 (3)
VII	17.45	**VIIa**	2.47 ± 0.60 (4)	–

[a] Relative scale with respect to 9-phenylfluorene standard, pK_{st} 18.5; pK values from [23].
[b] In parenthesis is given the number of determinations.

and basicity of these anions in the S_NAr reactions due to the solvation effect of the electron-acceptor groups in DMSO. Such effect was demonstrated for S_N2 reactions [4]. However the effect of enhanced solvation of the resonance-located electron-acceptor groups in N-anions **Ia–VIIa** apparently should not affect the relation between the nucleophilicity and basicity of these anions since a correlation exists between the basicity of N-anions in the gas phase and DMSO [6, 22, 23]. The lack of deviations from the correlation plot evidences the proportionality conservation in the effect of the enhanced solvation of the substituents [24].

The acidity of diarylamines **I–VII** in DMSO and the rate constants of the second order for the reaction of N-anions **Ia–VIIa** with hexafluorobenzene and pentafluoropyridine in DMSO at 25°C are presented in Table 1. Kinetic data show that the reactivity of hexafluorobenzene toward N-anions **Ia–VIIa** is lower than that of pentafluoropyridine within the total basicity range. Therewith the variation of rate constants is well consistent with Brønsted equations (2) and (3) (see the figure, plots *1* and *2*):

$$\log k(C_6F_6) = 0.14 \text{ p}K - 5.03; \; r\, 0.980, \; s\, 0.123, \; n\, 4 \quad (2)$$

$$\log k(C_5F_5N) = 0.34 \text{ p}K - 5.77; \; r\, 0.989, \; s\, 0.015, \; n\, 4 \quad (3)$$

The validity of Brønsted relations (2) and (3) evidences that sterical and solvation effects of substituents proportionally affect both the basicity and nucleophilicity of N-anions **Ia–VIIa**. At the same time the change in the value of the Brønsted factor β_{Nuc} from 0.14 to 0.34 in going from hexafluorobenzene to pentafluoropyridine shows that within the same range of nucleophile basicity variation the substitution selectivity grows with increasing electrophilicity of the substrate. The latter statement contradicts the reactivity–selectivity principle. It was shown earlier that the principle was valid for the $S_N Ar$ reactions [25]. However many examples exist that demonstrate no general applicability of the principle [26].

To analyze the cause of β_{Nuc} factor variation at further extension of the basicity range of the N-anions we invoked the previously obtained data on reactivity of arylamines N-anions toward hexafluorobenzene [27] and of aryl- and diarylamines N-anions toward 4-nitrofluorobenzene [6] in the range f Basicity variation of the N-anions from 15 to 25 pK units. The corresponding Brønsted plots are given on the figure (plots *3–5*). The data show that in the range of N-anions basicity variation from 15 to 25 pK units is

observed an increase in the factor β_{Nuc} in going from reaction of arylamines N-anions with 4-nitrofluorobenzene (figure, plot *4*, β_{Nuc} 0.28) to the reaction of the same anions with hexaflourobenzene (figure, plot *5*, β_{Nuc} 0.74). Thus in the same range of basicity variation the Brønsted factor again increases with the growing electrophilicity of the substrate (cf. plots *1* and *2*, *4* and *5* on the figure).

The comparison of Brønsted factors for the reactions of hexafluorobenzene with N-anions of diarylamines (β_{Nuc} 0.14) and arylamines (β_{Nuc} 0.74) suggests that within a vide range of basicity variation for these anions (~14 pK units) the Brønsted plots deviate from linearity (plots *1* and *5* on the figure). Apparently the deviation from linearity cannot be ascribed to the effect of different spatial reasons for N-anions of aryl- and diarylamines since the reactivity of these anions toward 4-nitrofluorobenzene is virtually the same in the same range of basicity variation (β_{Nuc} 0.24 and 0.28 [6], plots *3* and *4* on the figure).

The known cases of deviation of Brønsted plots from linearity in the nucleophilic substitution are due to the nonthermodynamical reasons: changes in the mechanism of reaction, solvation of nucleophiles, nature of the nucleophilic center in the nucleophile, and sterical effects [4, 28]. At minimal influence of structural and solvation characteristics the reactivity
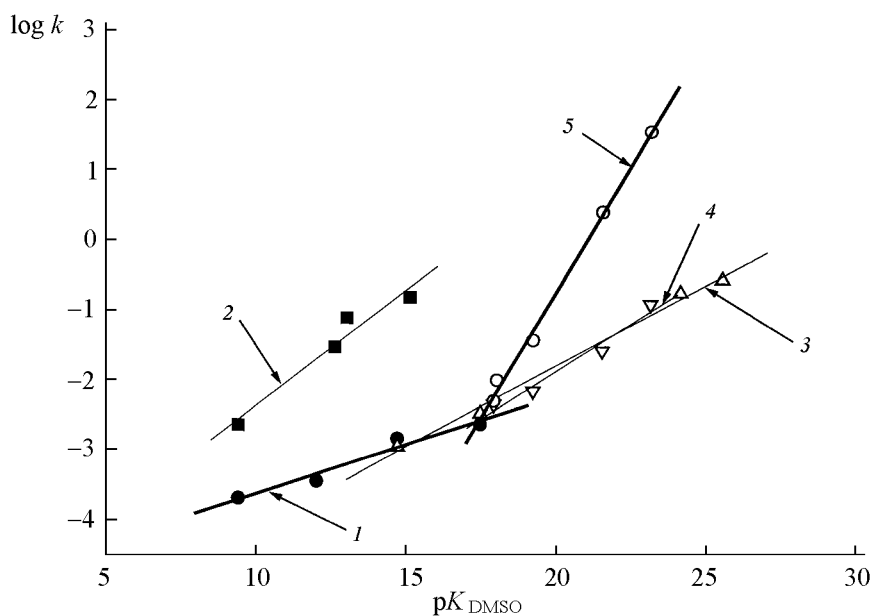
Brønsted plots for reactions of diarylamines N-anions **Ia, IIa, Va, VIIa** with hexafluorobenzene (plot *1*, β 0.14), of diarylamines N-anions **Ia, IIIa, IVa, VIa** with pentafluoropyridine (plot *2*, β 0.34), of diarylamines N-anions with *p*-nitrofluorobenzene (plot *3*, β 0.24) [6], of arylamines N-anions with *p*-nitrofluorobenzene (plot *4*, β 0.28) [6], and arylamines N-anions with hexafluorobenzene (plot *5*, β 0.74) [25] in DMSO at 25°C.

variation is described by a linear Brønsted plot. For instance, for reactions of alkyl halides with the C-, N-, O-, and S-anions the Brønsted plot is linear within a wide basicity range (~10–16 pK units [3, 4, 28, 29]) apparently due to the high internal barrier $\Delta G_0^{\neq}$ for S_N2 reactions [4, 28]. The expression for estimation of variations in the Brønsted factor may be derived by successive differentiating of Marcus equation (4) and equation (5) with respect to ΔG^0 [30]:

$$\Delta G^{\neq} = \Delta G_0^{\neq} + 1/2 - \Delta G^0 + (\Delta G^0)^2/16\Delta G_0^{\neq}, \quad (4)$$

where $\Delta G^{\neq}$ is the free activation energy, ΔG^0 is the free energy of reaction, $\Delta G_0^{\neq}$ is the internal barrier or the free activation energy at $\Delta G^0 = 0$. Then

$$\beta_{Nuc} = 1/2 + \Delta G^0/8\Delta G_0^{\neq}, \quad (5)$$

$$\delta(\beta_{Nuc})/\delta(\Delta G^0) = 1/8\Delta G_0^{\neq}. \quad (6)$$

Equation (6) expresses the variation in β_{Nuc} as a function of the internal barrier of the reaction $\Delta G_0^{\neq}$. In reactions of hexafluorobenzene with each series of N-anions originating both from aryl- and diarylamines the Brønsted plots are valid (straight lines *1* and *5*, see figure) indicating the linear variation of the internal barrier $\Delta G_0^{\neq}$ as a function of the free energy of the reactions $\Delta G^{\neq}$ corresponding to both plots [31]. The observed increase in the value of β_{Nuc} factor with growing basicity of the N-anions in their reaction with hexafluorobenzene (plots *1* and *5*, see figure) may be interpreted proceeding from equation (6). It is known that a small $\Delta G_0^{\neq}$ value is characteristic of fast reactions with a high Brønsted factor [4, 8]. Assuming that the basicity with respect to carbon changes in parallel with the basicity with respect to hydrogen [3] we take the range of basicity variation of N-anions around 14 pK 40 units or 19 kcal mol^{-1} as estimate for the free energy of the reaction $\Delta G^{\neq}$. This estimation is fairly approximate since the basicity of the charged anions with respect to carbon is known to be higher than their basicity with respect to hydrogen [32]. As follows from equation (6) the value of the internal barrier $\Delta G_0^{\neq}$ of the reaction between C_6F_6 and N-anions is equal to ~4 kcal mol^{-1} at change in the Brønsted factor of 0.74–0.14 = 0.6. This value is obviously underestimated since the real range of basicity variation of N-anions with respect to carbon should be considerably wider. Although the estimation of the internal barrier value is approximate we still can presume that the decrease in the value of the internal barrier $\Delta G_0^{\neq}$ with growing velocity of reaction the between

N-anions and hexafluorobenzene should result in a notable increase in the β_{Nuc} factor and to deviation from linearity in the plot of $\Delta G^{\neq}$ versus ΔG^0. Consequently the deviation from linearity of the Brønsted plot for reactions of aryland diarylamines anions with C_6F_6 may be due to the significant change in the values of internal barriers, i.e. to the dissimilar structure of the transition state in both reactions (plots *1* and *5*, see figure). In the faster reaction of C_6F_6 with arylamines N-anions (β_{Nuc} 0.74) the degree of charge transfer from the nucleophile to the substrate is higher than in the same reaction with the N-anions of diarylamines (β_{Nuc} 0.14) [33]. This statement is confirmed by a greater sensitivity of the logarithms of the rate constants in reactions of C_6F_6 with N-anions of arylamines to their redox potentials than to the redox potentials of diarylamines N-anions [14]. Thus to the higher β_{Nuc} value corresponds a greater sensitivity of the reaction rate to variation in the redox potentials of anions, and at the limiting value $\beta_{Nuc} \approx 1$ [3] we can expect that the reaction mechanism $S_N Ar$ will transform into SET mechanism (cf. [23]).

EXPERIMENTAL

IR spectra were recorded on UR-20 spectrophotometer from 1% solutions of compounds in $CHCl_3$, CCl_4 or from KBr pellets containing 0.25% of compound. ^{1}H and ^{19}F NMR spectra were registered on spectrometers Varian 56/60 A, Bruker WP 200 SY and AC 200, references TMS and hexafluorobenzene respectively. Mass spectra were measured on Finnigan Mat 8200 instrument at ionizing energy 70 eV, temperature in the ionizing chamber 100–200°C. The reaction mixtures were analyzed by GLC on HP5890 and LKhM devices (thermal conductivity detector, ramp from 50 to 270°C at 10 deg min^{-1}, stationary phase SKTFT-803 on Chromaton HMDC-N, carrier gas helium, flow rate 60 ml min^{-1}; the quantitative analysis of the reaction mixtures was carried out by internal normalizing procedure, the components were identified by comparison with authentic samples.

Commercial DMSO was purified and dried by vacuum distillation on CaH_2 at $10^{-3} \times 10^{-4}$ mm, DMF was distilled in a vacuum on phosphorus pentoxide as described in [34]. Commercial sodium hydride before use was washed with anhydrous hexane and dried under inert atmosphere. Commercial hexafluorobenzene before use was dried over molecular sieves. Commercial bromobenzene was distilled in a vacuum before use. The copper powder was prepared as described in [35]. Commercial 4-nitrodiphenylamine

(**VII**) was before use recrystallized from ethanol; *N*-(4-tetrafluoropyridyl)pentafluoroaniline (**I**), 4-chlorononafluorodiphenylamine (**II**), decafluorodiphenylamine (**III**), 4-methylnonafluorodiphenylamine (**IV**), 4-cyano-2,3,5,6-tetrafluorodiphenylamine (**V**), di-*N,N'*-(4-tetrafluoropyridyl)pentafluoroaniline (**XII**), 9-carbomethoxyfluorene (**XV**) were obtained by known procedures; their physical constants are consistent with the published data [6, 27, 36, 37].

N-(2,3,5,6-Tetraflyoropyridyl)aniline (VI). To a suspension of 0.26 g (0.108 mmol) of sodium hydride in 2 ml of DMF was added while stirring and at 20–25°C a solution of 2.73 g (0.162 mmol) of aniline in 3 ml of DMF. The addition continued for 1 h. Then was added 0.162 mmol of pentafluoropyridine. The reaction mixture was left to stand for 2 h, then it was diluted with ether, neutralized with 5% HCl, extracted with ether, the extract was washed with water and dried with $MgSO_4$. After evaporating the solvent the residue contained 2.21 g (84%) of compound **VI** (GLC data). By recrystallization from petroleum ether (bp 40–70°C) followed by sublimation at 90°C/2–3 mm we obtained 1.44 g (55%) of compound **VI**, mp 92–93°C. IR spectrum (CHCl₃, ν, cm⁻¹): 973 s (C–F), 1484 s (F-substituted arom. ring), 3416 m (NH). ¹H NMR spectrum (DMSO, δ, ppm): 7.02–7.12 m (3H, $H^{2,4,6}$), 7.25–7.31 m (2H, $H^{3,5}$), 9.40 s (1H, NH). ¹⁹F NMR spectrum external reference C_6F_6, DMSO, δ_F, ppm): 12.69 m (2F, $F^{3,5}$), 71.20 m (2F, $F^{2,6}$). Elemental composition and molecular weight were determined from high-resolution mass spectrum. Found: *M* 242.04689. $C_{11}H_6F_4N_2$. Calculated: *M* 242.04670.

N-(2,3,5,6-Tetraflyoropyridyl)decafluorodiphenylamine (VIII). Into a four-neck flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel was charged 0.08 g (3.16 mmol) of sodium hydride, 2 ml of DMF, and at stirring was added to the suspension within 40 min a solution of 1 g (2.87 mmol) of decafluorodiphenylamine (**III**) in 5 ml of DMF at 20–25°C. Then to the reaction mixture was added 0.97 g (5.74 mmol) of pentafluoropyridine, and the mixture was heated to 80°C. The reaction mixture was maintained at this temperature for 2 h 40 min, then cooled to room temperature, neutralized with 5% HCl, extracted with ether, the extract was washed with water, and dried on magnesium sulfate. The residue after evaporating the solvent (1.24 g) was recrystallized from CCl_4. We obtained 0.68 g (48%) of compound **VIII**, mp 117–118°C. IR spectrum (CCl₄, ν, cm⁻¹): 1000 s (C–F), 1525 s (F-substituted arom. ring).

¹⁹F NMR spectrum (CHCl₃, δ_F, ppm): 1.90 m (4F, $F^{3',5'}$), 9.18 m (2F, $F^{4'}$, $J_{2',4'}$ 19 Hz), 9.58 m (2F, $F^{3,5}$), 14.36 m (4F, $F^{2',6'}$), 73.73 m (2F, $F^{2,6}$). Found, %: C 40.34; F 53.56; N 5.45. $C_{17}F_{14}N_2$. Calculated, %: C 40.96; F 53.41; N 5.62.

N-(4-Chloro-2,3,5,6-tetraflyorophenyl)decafluorodiphenylamine (IX). Into a four-neck flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel was charged 0.206 g (8.58 mmol) of sodium hydride, 5 ml of DMF, and at stirring was added to the suspension within 1 h a solution of 1 g (2.87 mmol) of decafluorodiphenylamine (**III**) and 1.16 g (5.72 mmol) of pentafluorochlorobenzene in 15 ml of DMF at 20–25°C. Then the reaction mixture heated to 90°C and maintained at this temperature for 3 h, then cooled to room temperature, neutralized with 5% HCl, extracted with ether, the extract was washed with water, and dried on $CaCl_2$. The residue after the solvent was distilled off (1.45 g) contained according to GLC 5% of compound **IX**. By TLC on a glass plate 20×20cm, SiO_2, eluent CCl_4, we isolated 0.08 g of a mixture containing 0.33 g (49%) of compound **IX**, yield 2.6% (GLC), mp 124–126°C (sublimed at 130°C/2–3 mm). ¹⁹F NMR spectrum (CHCl₃, δ_F, ppm): 1.23 m (6F, $4F^{3',5'}$, $2F^{3,5}$), 6.87 m (2F, $F^{4'}$), 13.34 m (6F, $4F^{2',6'}$, $2F^{2,6}$). Elemental composition and molecular weight were determined from high-resolution mass spectrum. Found: *M* 530.94879. $C_{18}H_9F_5N_2O_2$. Calculated: *M* 530.94935.

N-(4-Cyano-2,3,5,6-tetraflyorophenyl)pentafluorodiphenylamine (X). Into a stainless steel ampule was charged 0.2 g (0.562 mmol) of *N*-(4-cyano-2,3,5,6-tetraflyorophenyl)pentafluoroaniline (**V**), 1 ml of bromobenzene, and 0.12 g (1.87 mmol) of copper powder. The ampule was heated on metal bath at 240–245°C for 43 h. The reaction mixture was cooled to room temperature, filtered, the filtrate was evaporated, and the residue was subjected to chromatography (Al_2O_3, eluent CHCl₃). We obtained 0.22 g (9%) of compound X, mp 172–174.5°C. ¹H NMR spectrum (DMSO-d_6, δ, ppm): 7.09–7.50 m (5H, H arom). ¹⁹F NMR spectrum (external reference C_6F_6, DMSO-d_6, δ_F, ppm): 0.49 m (2F, $F^{3',5'}$), 6.41 m (1F, $F^{4'}$), 15.64 m (2F, $F^{2,6}$), 17.79 m (2F, $F^{2',6'}$), 28.52 m (2F, $F^{3,5}$). Elemental composition and molecular weight were determined from high-resolution mass spectrum. Found: *M* 432.03089. $C_{19}H_5F_9N_2$. Calculated: *M* 432.03089.

N-(4-Nitrophenyl)pentafluorodiphenylamine (XI). Into a four-neck flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping

funnel was charged 0.08 g (3.3 mmol) of sodium hydride, 1.01 g (5 mmol) of hexafluorobenzne, 1 ml of DMF, and at stirring was added to the suspension within 5 min a solution of 0.2 g (0.99 mmol) of 4-nitrodiphenylamine (**VII**) in 2 ml of DMF and the reaction mixture was maintained at 20–25°C for 1.5 h. The reaction mixture was neutralized with 5% HCl and acidified to weakly acid reaction by litmus. The reaction mixture was left overnight, the separated precipitate was filtered off, washed with water, and dried. From 0.15 g of the precipitate was isolated by TLC (Al$_2$O$_3$, CHCl$_3$) 0.099 g (28%) of compound **XI**, mp 266–268°C. IR spectrum (CHCl$_3$, ν, cm^{-1}): 1005 s (C–F), 1317 s (NO$_2$), 1512 s (F-substituted arom. ring), 1588 s (NO$_2$). ^{1}H NMR spectrum (acetone-d_6, δ, ppm): 7.12 m (2H, H^{2,6}), 7.32–7.52 m (5H, H arom.), 8.14 m (2H, H^{3,5}, $J_{2,3}$ 9 Hz).

^{19}F NMR spectrum (acetone-d_6, δ_F, ppm): 1.05 m (2F, F^{3,5}), 6.26 m (1F, F^4), 17.48 m (2F, F^{2,6}). Elemental composition and molecular weight were determined from high-resolution mass spectrum. Found: M 380.0563. C$_{18}$H$_9$F$_5$N$_2$O$_2$. Calculated: M 380.0584.

N,N-(4-Methyl-2,3,5,6-tetrafluorophenyl)-(2',3',5',6'-tetrafluoropyridyl)pentafluoroaniline (XIII).

Into a glass reactor connected to a vacuum line were placed glass balls containing sealed in a vacuum precisely weighted amounts of sodium hydride (0.0325 g, 1.35 mmol), 4-methylnonafluoro-diphenylamine (0.202 g, 586 mmol), pentafluoro-pyridine (0.198 g, 1.17 mmol), and 65% HNO$_3$. The reactor was sealed, evacuated to 10^{-4} mm Hg, 7 ml of DMF was added, and then the reactor was sealed off the vacuum line. The glass ball were crushed in succession to produce N-anion, then to react it with pentafluoropyridine for 2 h at room temperature. Finally the mixture was neutralized with the 65% HNO$_3$, the system was opened to the atmosphere, the reaction mixture was extracted with ether, the extract was washed with water, and dried on MgSO$_4$. The residue after evaporation of the ether contained according to GLC 0.23 g (79%) of compound XIII. The product was isolated by column chromatography (Al$_2$O$_3$, eluent 5 vol% CHCl$_3$ in CCl$_4$). We obtained 0.083 g (17%) of compound **XIII**, mp 101.5 × 103°C. IR spectrum (CHCl$_3$, ν, cm^{-1}): 1000 s (C–F), 1500 s (F-substituted arom. ring). ^{1}H NMR spectrum (CCl$_4$, δ, ppm): 2.93 s (3H, CH$_3$). ^{19}F NMR spectrum (CCl$_4$, δ_F, ppm): 1.4 m (2F, F$^{3'',5''}$), 8.3 m (1F, F$^{4''}$), 9.1 m (2F, F$^{3',5'}$), 12.2 m (2F, F^{2,6}), 14.3 m (2F, F$^{2'',6''}$), 20.1 m (2F, F^{3,5}), 73.5 m (2F, F$^{2',6'}$). Elemental composition and molecular weight were determined from high-resolution mass spectrum.

Found: M 494.0088. C$_{18}$H$_3$F$_{13}$N$_2$. Calculated: 494.0089.

N,N-Di-[4-(2,3,5,6-tetrafluoro)pyridyl]aniline (XIV).

To a suspension of 0.042 g (1.75 mmol) of sodium hydride in 1 ml of DMF was added dropwise within 20 min a solution of 0.2 g (0.83 mmol) of N-(2,3,5,6-tetraflyoropyridyl)aniline (**VI**) in 3 ml of DMF; then was added a solution of 0.28 g (1.66 mmol) of C$_5$F$_5$N in 1 ml of DMF, and the mixture was left standing at 20–25°C for 2 h. The reaction mixture was diluted with ether, neutralized with 5% HCl, extracted with ether, the extract was washed with water, and dried on MgSO$_4$. On evaporating the solvent the residue according to GLC contained 0.22 g (69%) of compound **XIV** that was separated by TLC (SiO$_2$, eluent 10 vol% CHCl$_3$ in CCl$_4$) We obtained 0.17 g (52%) of compound **XIV**, mp 179–181°C. IR spectrum (CHCl$_3$, ν, cm^{-1}): 978 s (C–F), 1500 s (F-substituted arom. ring). ^{1}H NMR spectrum (acetone, δ, ppm): 7.37 m (5H, H arom.). ^{19}F NMR spectrum (acetone, δ_F, ppm): 15.7 m (2F, F^{3,5}), 73.0 m (2F, F$^{2.6}$). Elemental composition and molecular weight were determined from high-resolution mass spectrum. Found: M 391.03552. C$_{16}$H$_5$F$_8$N$_3$. Calculated: M 391.03561.

1,4-Bis[N,N-(phenyl-4-nitrophenyl)]tetrafluoro-phenylenediamine (XVI).

Into a four-neck flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel was charged 0.336 g (14 mmol) of sodium hydride, 1 ml of DMF, and at stirring was added dropwise to the suspension within 5 min a solution of 1 g (4.67 mmol) of 4-nitrodi-phenylamine (**VII**) in 5 ml of DMF. Then was added dropwise within 5 min a solution of 1.74 g (9.4 mmol) of hexafluorobenzene in 4 ml of DMF. The mixture was held at 20–25°C for 5 h 50 min. Then to the reaction mixture was added 5% HCl to slightly acid reaction toward litmus, the products were extracted into dichloromethane, the extract was washed with water, and dried with CaCl$_2$. The liquid residue after evaporation of the solvent (4.46 g) was diluted with water, the separated precipitate was filtered off and dried. After double recrystallization of the precipitate from CHCl$_3$ we obtained 0.74 g (55%) of compound **XVI**, mp 274.5–276°C. IR spectrum (CHCl$_3$, ν, cm^{-1}): 1315 s (NO$_2$), 1500 s (F-substituted arom. ring), 1575 s (NO$_2$). ^{1}H NMR spectrum (CDCl$_3$, δ, ppm): 6.3 m (4H, H^{2,6}), 8.10 m (4H, H^{3,5}, $J_{2,3}$ 10 Hz), 7.31–7.34 m (10H, H arom.). ^{19}F NMR spectrum (CDCl$_3$, δ_F, ppm): 16.28 s (4F, F$^{2',3',5',6'}$). Elemental composition and molecular weight were determined from high-resolution

mass spectrum. Found: M 574.1231. $C_{30}H_{18}F_4N_4O_4$. Calculated: M 574.1264.

9-Carbomethoxy-9-(4-tetrafluoropyridyl)-fluorene (XVII). To a suspension of 0.11 g (4.6 mmol) of sodium hydride in 1.5 ml of DMSO in an argon flow was added dropwise within 25 min at stirring a solution of 0.5 g (2.2 mmol) of 9-carbomethoxyfluorene (**XV**) in 3.5 ml of DMSO. Then was added 0.76 g (4.5 mmol) of pentafluoropyridine in 2 ml of DMSO, and the mixture was maintained at 20–25°C for 2 h. Then the reaction mixture was neutralized with 5% HCl, extracted with ether, the extract was washed with water and dried with $MgSO_4$. On removing the solvent the residue (1.07 g) contained 81% of the product (GLC). On recrystallization from petroleum ether (bp 70×100°C) we obtained 0.42 g (53%) of compound **XVII**. mp 153–155°C. ^{1}H NMR spectrum (CDCl$_3$, δ, ppm): 3.67 s (3H, CH$_3$), 7.31–8.03 m (8H, H arom). ^{19}F NMR spectrum (CDCl$_3$, δ_F, ppm): 24.2 m (2F, F^{3,5}), 71.6 m (2F, F^{2,6}). Found, %: C 63.97; H 2.94; F 20.14; N 3.72. $C_{20}H_{11}F_4NO_2$. Calculated, %: C 64.34; H 2.95; F 20.37; N 3.75.

Generation of sodium salt of anion from N-(4-tetrafluoropyridyl)pentafluoroaniline (Ia). Into an NMR tube flushed with argon was charged 0.0299 g (0.09 mmol) of compound **I** and 0.3 ml of DMSO, and the ^{19}F NMR spectrum was registered. Then was added 0.0035 g (0.0648 mmol) of sodium methylate, and the reaction mixture was left standing for 3 h. Then the ^{19}F NMR spectrum was again registered. Trifluoromethylbenzene was used as internal reference. The parameters of the spectra are given in Table 2.

Generation of sodium salts of anions from compounds III, IV, VI, XV in DMSO. The experiments were carried on a glass sealed system connected to a vacuum line and evacuated to 1×10^{-4} mm Hg. To a suspension of 1.3 mmol of sodium hydride in 0.5 ml of DMSO was added 0.32 mmol of compound **III, IV, VI**, or **XV** at 20–25°C. The reaction mixture was kept for 3h, then transferred into an NMR tube, the tube was sealed off from the vacuum system, and the NMR spectra were registered. The system was connected to air, the residue of the reaction mixture was neutralized with 5% HCl, extracted with ether, and the extract was dried with $MgSO_4$. On evaporating the solvent the residue according to GLC contained the initial compounds **III, IV, VI**, and **XV**. The ^{1}H and ^{19}F NMR spectra of compounds **III, IV, VI, XV** and their sodium salts **IIIa, IVa, VIa,** and **XVa** are presented in Table 2.

Generation of pairs of sodium salts of anions IIIa + IVa, IIIa + XVa, VIa + XVa in DMSO. The experiments were carried on a glass sealed system connected to a vacuum line and evacuated to 1×10^{-4} mm Hg. To a suspension of 2.56 mmol of sodium hydride in 2–2.5 ml of DMSO was added equimolar amounts (0.63 mmol each) of compounds **III + IV, III + XV**, or **VI + XV**. The reaction mixture was kept for 3 h at 20–25°C, then transferred into an NMR tube. From the ratio of the chemical shifts values of the corresponding atoms in the NMR spectra of the neutral compounds, their anions, and the mixtures was calculated the initial ratio of concentrations of the anions pairs: **IIIa/IVa** = 1.04, **IIIa/XVa** = 0.81, **VIa/XVa** = 0.93. Parameters of the spectra are given in Table 2.

Determination of rate constants for reactions of diarylamines I, II, V, VII with hexafluorobenzene, and of diarylamine III with pentafluoropyridine. General procedure. All experiments were carried out under argon atmosphere. Diarylamines and aryl-fluorides were taken in a molar ratio at initial concentration $(3–6) \times 10^{-2}$ mol l^{-1}, sodium hydride was used in excess, 2–3 mol per 1 mol of diarylamine. The rates were measured by potentiometric determination of fluoride ion with the use of lanthanum-fluoride electrode [38]. The weighed portions of reagents were placed into evacuated glass balls; the balls were charged into a glass reactor connected to a vacuum line, the reactor was evacuated to 1×10^{-4} mm Hg, solvent was added, and the reactor was sealed off the vacuum line. The glass balls were crashed in succession (first was generated the N-anion); the reaction mixture was kept for a definite time, and then the reaction was stopped by addition of 65% nitric acid. The reaction mixture was transferred from the reactor into a volumetric flask of 50 ml capacity and the volume was completed to 50 ml with distilled water. The rate constant (l mol^{-1} s^{-1}) was calculated by the equation for the second order reaction basing on the content of fluoride ion:

$$k = [2.303/\tau(a - b)]\log[b(a - x)/a(b - x)],$$

where a and b are initial concentrations of the reagents, mol l^{-1}, x is the concentration of the reaction product, mol l^{-1}, τ is reaction time, s.

In the calculations of the Brønsted factor β_{Nuc} were used the rate constants evaluated with accounting for the number of equivalent positions in the hexafluorobenzene: $k' = k/6$. The logarithms of the rate constants of the reaction are listed in Table 1.

Table 2. Parameters of ^{1}H and ^{19}F NMR spectra of compounds **I, III, IV, VI, XV** and N-anions thereof **Ia, IIIa, IVa, VIa, XVa** in DMSO at 25°C

Compound	^{19}F NMR spectra, δ_F, ppm, external reference C_6F_6			^{1}H NMR spectra[a], δ, ppm, external reference TMS		
	$2F^{2,6}$ $(2F^{2',6'})$	$2F^{3,5}$ $(2F^{3',5'})$	F^4	Aromatic protons	XH	R
$C_6F_5NHC_5F_4N$-4 (**I**)	16.47 (5.41)	1.73 (70.75)	7.11	–	9.84 s (1H, NH)	–
C_6F_5N-(Na+)C_5F_4N-4 (**Ia**)	14.12 (1.31)	0.20 (68.23)	3.47	–	–	–
$C_6F_5NHC_6F_5$ (**III**)	9.66	–1.36	–0.9	–	8.72 s (1H, NH)	–
$(C_6F_5)_2N$-Na+ (**IIIa**)	6.21	–3.37	–19.0	–	–	–
$C_6F_5NHC_6F_4CH_3$-p (**IV**)	9.1 (8.0)	–1.3 (17.1)	–3.1	–	8.77 s (1H, NH)	3.86 s (3H, CH_3)
C_6F_5N-(Na+)$C_6F_4CH_3$-p ((**IVa**))	7.3 (5.8)	–3.5 (15.5)	–20.2	–	–	2.81 s (3H, CH_3)
PhNHC$_5F_4N$-4 (**VI**)	12.69	71.20	–	7.29–7.36 m (2H, $H^{3,5}$), 7.06–7.16 m (3H, $H^{2,4,6}$)	9.44 s (1H, NH)	–
PhN-(Na+)C_5F_4N-4 (**VIa**)	3.23	62.07	–	7.04–6.97 m (2H, $H^{3,5}$), 6.59–6.67 m (3H, $H^{2,4,6}$)	–	–
9-CH_3CO_2Fl[b] (**XV**)	–	–	–	7.32–7.42 m (4H, $H^{2,3,6,7}$), 7.64–7.67 m (2H, $H^{1,8}$), 7.68–7.91 m (2H, $H^{4,5}$)	5.09 s (H^9)	3.70 s (3H, CH_3)
9-CH_3CO_2Fl-(Na+) (**XVa**)	–	–	–	6.85–6.92 m (2H, $H^{3,7}$), 7.14–7.22 m (2H, $H^{2,6}$), 7.95–7.99 m (2H, $H^{1,8}$), 8.00–8.40 m (2H, $H^{4,5}$)	–	3.81 s (3H, CH_3)
$(C_6F_5)_2N$-Na+ (**IIIa**) + C_6F_5N-(Na+)$C_6F_4CH_3$-p (**IVa**)	6.0 7.1 (6.0)	–3.5 –3.5 (15.4)	–20.3 –21.4	– –	–	– 2.84 s (3H, CH_3)
$(C_6F_5)_2N$-Na+ (**IIIa**) + 9-CH_3CO_2Fl-(Na+) (**XVa**)	7.60 –	–2.13 –	–14.7 –	– 6.83–7.31 m (4H, $H^{2,3,6,7}$), 7.78–8.34 m (4H, $H^{1,4,5,8}$)	– –	– 3.86 s (3H, CH_3)
PhN-(Na+)C_5F_4N-4 (**VIa**) + 9-CH_3CO_2Fl-(Na+) (**XVa**)	3.36 –	62.26 –	– –	6.65–6.89 m (3H, $H^{2,4,6}$), 7.04–7.42 m (2H, $H^{3,5}$) 6.89–7.04 m (2H, $H^{3,6}$), 7.04–7.42 m (2H, $H^{2,7}$), 7.92–8.12 m (2H, $H^{1,8}$), 8.02–8.48 m (2H, $H^{4,5}$)	– –	– 3.85 s (3H, CH_3)

[a] Proper value of intensity ratio. [b] Fl is fluorenyl.

The rate constants for each compound were measured at least three times. The lack in the reaction mixture of 1,4-bis[N,N'-(phenyl-4'-nitrophenyl]tetrafluorophenylenediamine (**XVI**) in reaction between 4-nitrodiphenylamine N-anion and hexafluorobenzene was checked by means of liquid chromatography ("Milichrom 2", 100% methanol, silasorb C_{18}) by adding an authentic sample of **XVI** into the reaction mixture.

Determination of rate constant for reaction of *N*-(4-tetrafluoropyridyl)pentafluoroaniline (I) with pentafluoropyridine. Glass balls containing weighed portions of reagents: 0.0239 g (0.0712 mmol) of

Table 3 Relative rates of reaction with pentafluoro-pyridine of anions **IIIa, IVa, VIa**, and **XVa** in DMSO at 25°C

N-anion no.	k_{rel}	n^{a}
IIIa	1.0	5 (±14.7)
IVa	2.7	5 (±14.7)
VIa	5.4	3 (±16.5)
XVa	22.0	3 (±4.7)

[a] n is number of experiments; deviations , % are given in parentheses.

compound **I**, 0.0117 g (0.0692 mmol) of pentafluoro-pyridine, 0.0038 g (0.0704 mmol) of sodium methyl-ate, and of 65% HNO_3, and 1.8 ml of DMSO were placed into a glass reactor connected to a vacuum line. The reactor was evacuated to 1×10^{-4} mm Hg and sealed off the vacuum line. By successive crushing of balls with reagents was first generated anion **Ia**, then the reaction mixture was maintained for a definite time (10–55 min), then neutralized with 65% HNO_3. The mixture in a volumetric flask was diluted with distilled water till precise volume of 50 ml, and the content of fluoride ion was determined. The rate constant was calculated by the equation for second order reactions. The calculation results are presented in Table 1.

Determination of relative reaction rate between diarylamines N-anions IIIa, IVa, and VIa and pentafluoropyridine. General procedure. To a suspen-sion of 2–2.7 mmol of sodium hydride in 2 ml of DMSO was added in an argon flow at stirring a solu-tion of equimolar amounts of compounds **III** and **IV**, **III** and **XV**, or **VI** and **XV** (0.5 mmol each) in 4–5 ml of DMSO. The reaction mixture was stirred for 2 h at 25°C, diluted with ether, neutralized with 5% HCl, and extracted with ether. The ether extract was washed with water and dried on $MgSO_4$. The residue after ether evaporation was analyzed by GLC. The relative rates of reaction within each pair, e.g., **III** and **IV**, were calculated by equation (7) [39]:

$$k_{III}/k_{IV} = \log([III a]_0/[III a]_t)/\log([IV a]_0/[IV a]_t), \quad (7)$$

where $[III a]_0$ and $[IV a]_0$ are initial concentrations of anions in the mixture calculated with accounting for the ratio of anions in the mixture determined by NMR data (Table 2), $[III a]_t$, $[IV a]_t$ are anion con-centrations at the end of reaction, mol l^{-1}.

The yield of reaction products was estimated from GLC data by adding the authentic samples. The results of relative rate determinations are given in Table 3. The determination of the relative rate of reaction between N-anion **VIa** and pentafluoro-pyridine was determined by comparison with the anion **XVa** of 9-carbomethoxyfluorene since with anion **IVa** the retention times of reaction products **XIII** and **XIV** coincided preventing the evaluation of their yields. The rate constants of anions **IVa** and **VIa** in reaction with pentafluoropyridine listed in Table 1 were calculated using the rate constant determined in reaction of N-anion **IIIa** with pentafluoropyridine.

REFERENCES

1. Harris, J.M. and McManus, S.P., *Nucleophilicity,* Harris, J.M. and McManus, S.P., Eds., *Adv. Chem. Ser. No. 215*, Washington, DC, 1987, pp. 1–20.
2. Trushkov I.V., Chuvylkin N.D., Koz'min A.S., and Zefirov N.S., *Izv. Akad. Nauk, Ser. Khim.,* 1995, no. 5, pp. 804–826.
3. Bordwell, F.G., Cripe, T.A., and Hughes, D.L., *Nucleophilicity,* Harris, J.M., and McManus, S.P., *Adv. Chem., Ser. No. 215,* Washington, DC, 1987, pp. 137–153.
4. Bordwell, F.G., Branca, J.C., and Cripe, T.A., *Isr. J. Chem.,* 1985, vol. 26, no. 13, pp. 357–366.
5. Bordwell, F.G. and Hughes D.L., *J. Am. Chem. Soc.,* 1986, vol. 108, no. 19, pp. 5991–5997.
6. Vlasov V.M. and Os'kina I.A., *Zh. Org. Khim.,* 1994, vol. 30, no. 10, pp. 1507–1512.
7. Dixon, J.E. and Bruice, T.C., *J. Am. Chem. Soc.,* 1972, vol. 94, no. 6, pp. 2052–2056.
8. Knowles, J.R., Norman, R.O.C., and Prosser, J.H., *Proc. J. Chem. Soc.,* 1961, pp. 341–342.
9. Satpathy, K.K. and Nayak, P.L., *J. Ind. Chem. Soc.,* 1972, vol. 49, no. 6, pp. 615–620.
10. Kingsbury, G.A., *J. Org. Chem.,* 1964, vol. 29, no. 11, pp. 3262–3270.
11. Leahy, G.D., Liveris, M., Miller, J., and Par-ker, A.J., *Austral. J. Chem.,* 1956, vol. 9, pp. 382–390.
12. Ryan, J.J. and Humffray, A.A., *J. Chem. Soc.,* 1967, B, no. 12, pp. 1300–1305.
13. Crampton, M.R. and Willison, M.J., *J. Chem. Soc., Perkin Trans. II,* 1974, no. 3, pp. 238–241.
14. Vlasov, V.M., Os'kina, I.A., and Starichenko, V.F., *Zh. Org. Khim.,* 1997, vol. 33, no. 5, pp. 720–724.
15. Bolton, R. and Sandall, J.P.B., *J. Chem. Soc., Perkin Trans. II,* 1978, no. 12, pp. 1288–1292; Briner, J.P., Liveris, M., Lutz, P.G., and Miller, J., *J. Chem. Soc.,* 1954, no. 4, pp. 1265–1266;

Shein, S.M. and Rodionov, P.P., *Kinetika i kataliz,* 1973, vol. 14, no. 5, pp. 1128–1133.

16. Bartoli, J. and Todesco, P.E., *Acc. Chem. Res.,* 1977, vol. 10, no. 4, pp. 125–132.

17. Birchall, J.M., Green, M., Haszeldine, R.N., and Pitts, A.D., *Chem. Commun.,* 1967, no. 7, pp. 338–339.

18. Suhr, H., *Chem. Ber.,* 1964, vol. 97, no. 12, pp. 3277–3283; Miller, J. and Parker, A.J., *J. Am. Chem. Soc.,* 1961, vol. 83, no. 1, pp. 117–123.

19. Rodionov, P.P., Nekhoroshev, S.A., and Kollegov, V.F., *Kinetika i kataliz,* 1982, vol. 23, no. 3, pp. 558–562.

20. Chambers, R.D., Close, D., and Willams, D.L.H., *J. Chem. Soc., Perkin Trans. II,* 1980, no. 5, pp. 778–780; Chambers, R.D., Musgrave, W.K.R., Waterhouse, J.S., and Williams, D.L.H., *Chem. Commun.,* 1974, no. 6, pp. 239–240.

21. Galkin, V.I. and Cherkasov, V.I., *Reakts. Sposobn. Org. Soed.,* 1981, vol. 18, no. 1, pp. 111–132.

22. Koppel, I.A., Koppel, J., Maria, P.-C., Gal, J.-F., Notario, R., Vlasov, V.M., and Taft, R.W., *Int. J. Mass Spectr. Ion Processes,* 1998, vol. 175, no. 1, pp. 61–69.

23. Vlasov, V.M., Os'kina, I.A., Landini, D., and Maiya, A., *Izv. AN. Ser. Khim.,* 1995, no. 12, pp. 2315–2319.

24. Taft, R.W. and Bordwell, F.G., *Acc. Chem. Res.,* 1988, vol. 21, no. 12, pp. 463–469.

25. Gandler, J.R., Setiarahardjo, I.U., Tufon, C., and Chen, C., *J. Org. Chem.,* 1992, vol. 57, no. 15, pp. 4169–4173.

26. Pross, A., *Advances in Physical Organic Chemistry,* 1977, vol. 14, pp. 69–132; Ta-Shma, R. and Rappoport, Z., *J. Am. Chem. Soc.,* 1983, vol. 105, no. 19, pp. 6082–6095; Buncel, E., *J. Chem. Educ.,*

1987, vol. 67, no. 6, pp. 475–480; Johnson, C.D. and Stratton, B., *J. Chem. Soc. Perkin Trans. II,* 1988, pp. 1903–1907; Exner, O., *J. Chem. Soc. Perkin Trans. II,* 1993, pp. 973–979.

27. Vlasov, V.M. and Os'kina, I.A., *Izv. SO Akad. Nauk SSSR, Ser. Khim.,* 1984, no. 4, pp. 102–113.

28. Bordwell, F.G. and Hughes, D.L., *J. Org. Chem.,* 1982, vol. 47, no. 17, pp. 3224–3232.

29. Bordwell, F.G. and Hughes, D.L., *J. Am. Chem. Soc.,* 1984, vol. 106, no. 11, pp. 3234–3240; *J. Org. Chem.,* 1980, vol. 45, no. 16, pp. 3314–3320.

30. Marcus, R.A., *J. Phys. Chem.,* 1968, vol. 72, no. 13, pp. 891–892.

31. Tarkka, R.M., Park, W.K.C., Liu, P., Buncel, E., and Hoz, S., *J. Chem. Soc., Perkin Trans. II,* 1994, no. 12, pp. 2439–2444.

32. Crampton, M.R., *J. Chem. Soc.,* 1971, B, no. 11, pp. 2112–2116.

33. Pross, A., *J. Org. Chem.,* 1984, vol. 49, no. 10, pp. 1811–1818; Hoz, S., *Acc. Chem. Res.,* 1993, vol. 26, no. 2, pp. 69–74.

34. Weisberger, A., *Technique of Organic Chemistry,* New York: Interscience Publishers, 1955.

35. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemical Substances), Moscow: Khimiya, 1974, p. 230.

36. Vlasov, V.M. and Yakobson, G.G., *Zh. Org. Khim.,* 1981, vol. 17, no. 10, pp. 2192–2201.

37. Wislicenus, W. and Mocker, W., *Chem. Ber.,* 1913, vol. 46, pp. 2772–2793.

38. Tsingarelyan, R.D., Kan'shina, E.A., and Tabakova, O.M., *Zh. Analit. Khim.,* 1981, vol. 36, no. 8, pp. 1557–1563.

39. *Investigation of Rates and Mechanisms of Reactions,* Bernasconi, C.F., Ed., New York: Wiley-Intersci. Publ., 1986, p. 203.