EFFECTS OF SUBSTITUENTS IN ACID-CATALYZED CLAISEN AMINO REARRANGEMENT

I. B. Abdrakhmanov, Z. N. Saraeva, N. G. Nigmatullin, V. D. Komissarov, and G. A. Tolstikov UDC 541.124:541.127:542.91:547.551.2

A series of $4-R^2-N-R^1-N-(1-methyl-2-butenyl)-$ and $4-R^2-N-R^1-2-(1-methyl-2-butenyl)$ anilines was synthesized. The rate constants of rearrangement and elimination of the hydrochlorides of the $4-R^2-N-R^1-N-(1-methyl-2-butenyl)$ anilines in nitrobenzene were measured at 110 and 130°C. The correlation equations which describe the effect of the nature of the substituents on the reactivity of the substrate in these reactions and the selectivity of their occurrence were established. A mechanism of the processes was proposed.

The corresponding 2-allylaniline is formed, and aniline and diene parallelly accumulate as a result of acid-catalyzed Claisen amino rearrangement [1]. The effect of the structure of the substrate on the ratio of the two directions of the process has been insufficiently investigated [2, 3]. A series of $4-R^2-N-R^1-N-(1-methyl-2-butenyl)$ anilines (A) was synthesized, and the dependence of the rate constants k_1 , k_2 on the nature of substituents R^1 , R^2 was investigated in the present study



 $R^1 = H$, $R^2 = H$ (Ia, b), Me (IIa, b), MeO (IIIa, b), Cl (IVa, b); $R^2 = H$, $R^1 = Me$ (Va, b), Et (VIa, b), Pr (VIIa, b), i-Pr (VIIIa, b), i-Bu (IXa, b), t-Bu (Xa, b), PhCH₂ (XIa, b).

EXPERIMENTAL

N-alkylanilines were prepared from anilines and alkyl halides by the method in [4]. Compounds (Ia)-(VIIa) were synthesized from the corresponding $4-R^2-N-R^1$ -anilines and 4-chloro-2-pentene at 25°C. While stirring, 0.1 mole of 4-chloro-2-pentene was added to 0.5 mole of aniline over 1 h. The reaction mixture was stirred for 1 h, treated with a 20% aqueous solution of NaOH, and the organic layer was separated and dried over KOH. The products were separated by vacuum distillation.

(VIIIa)-(XIa) were synthesized according to [5].

Hydrochlorides of (Ia)-(XIa) were prepared by passing gaseous HCl in solutions of (A) in hexane. The precipitated sediment was washed three times with hexane, filtered off, and vacuum dried.

For preparation of $4-R^2-N-R^1-2-(1-methyl-2-butenyl)$ anilines (Ib)-(XIb), 0.1 mole of 4chloro-2-pentene was added to 0.5 mole of $4-R^2-N-R^1$ -aniline at 20°C while stirring. The reaction mixture was heated to 110-180°C and held for 0.5-6 h (as a function of the nature of the

Institute of Chemistry, Bashkir Scientific Center, Ural Branch, Academy of Sciences of the USSR, Ufa; Bashkir Institute of Agriculture, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2303-2308, October, 1989. Original article submitted July 27, 1988.

TABLE	1.	IR	and	PMR	Spectra	of	the	Compounds	Obtained

Com- pound	Bp, °C (p, mm Hg) IR spectrum) V, cm ⁻¹	PMR spectrum δ, ppm
		1	
(Ia)	101-103(1)	980, 1520, 1610, 3400	1,15 d $(3H, CH_3)$, 1,58 d $(3H, CH_3)$, 3.27 s $(1H, NH)$, 3,80 m $(1H, CH)$, 5,40 m $(2H, CH=CH)$,
(II <i>a</i>)	112-113(4)	980, 1625, 3420	1.08 d (3H, CH ₃), 1.53 d (3H, CH ₃), 2.10 s (3H, CH ₃), 3.13s (1H, NH), 3.74 m (1H, CH),
(IIIa)	137-139(10)	975, 1620, 3370	5,35 m (2H, CH=CH), 6.78 m (4H, Ar) 1,13 d' (3H, CH ₃), 1.56 d' (3H, CH ₃), 3.30 m (1H, NH), 3.53 s (3H, OCH ₃), 3.65 m (1H, CH),
(IVa)	140 (3)	975, 1605, 3410	5,31 m ⁻ (2H, CH=CH), 6,40 m ⁻ (4H, Ar) 1,13 d (3H, CH ₃), 1,57 d (3H, CH ₃), 3,32 br.s (1H, NH), 3,75 m (1H, CH), 5,35 m (2H, CH=
(Va)	135-138 (33)	980, 1520, 1610	=CH), 6_{17} -7,0 m (4H, Ar) 1,12 d (3H, CH ₃), 1,63 d (3H, CH ₃), 2,58 s (3H, CH ₃), 4,30 m (1H, CH), 5,45 m (2H, CH=CH),
(VIa)	99-100(2)	980, 1510, 1600	6,58-6,95 m (5H, Ar) $0,94 s (3H, CH_3), 1,05d (3H, CH_3), 1,54d (3H, CH_3), 3,02 qu (2H, CH_2), 4,46 m (1H, CH).$
(VIIa)	108-110(2)	980, 1600, 2885	5,36 m (2H, CH=CH), 6,50-6,90 m (5H, År) 0,87 t (3H, CH ₃), 1,22 d (3H, CH ₃), 1,70 m (5H, CH ₂ , CH ₃), 3,03 m (2H, CH ₂ -N), 2,87-3,12 m (1H, CH), 5,48 m (2H, CH=CH), 6,53-7,05
(VIIIa)	105(1)	980, 1370, 1380, 1600	(5H, Ar) 1,12 d (6H, 2CH ₃), 1,17 d (3H, CH ₃), 1,66d (3H, CH ₃), 3,50-4,17 m (2H, 2CH), 5,53 m (2H,
(IXa)	110-112(1)	980, 1600, 2890	CH=CH), $6,67-7,07 \text{ m}$ (5H, Ar) 0,87 d (6H, 2CH ₃), 1,17 d (3H, CH ₃), 1,55- 2,00 m (4H, CH, CH ₃), 2,78 d (2H, CH ₂),
			4,00-4,40 m (1H, CH), 5,50 m (2H, CH=CH), 6,62-7,22 m (5H, Ar)
(Xa)	100-102(2)	985, 1370, 1400, 1600	$(3,03 \text{ d} (3\text{H}, \text{CH}_3), 1.17 \text{ s} (9\text{H}, 3\text{CH}_3), 1.60 \text{ d} (3\text{H}, \text{CH}_3), 3.97 \text{ m} (1\text{H}, \text{CH}), 5.50 \text{ m} (2\text{H}, \text{CH} = -\text{CH}), 6.02, 7.22 \text{ m} (5\text{H}, 4\text{N})$
(XIa)	170-175(4)	990, 1510, 1600, 2940	$(23 d (3H, CH_3), 1.65 d (3H, CH_3), 4.33 s (2H, CH_2), 4.13-4.63 m (1H, CH), 5.52 m (2H, CH=0.04), 6.48 - 5.22 m (4H, CH) = 0.48 - 5.22 m (4H, $
(Љ)	104-106(2)	980, 1625, 3360, 3440	= CH), $0.40 - 1.32$ m (10H, 2AF) 1.22 d (3H, CH ₃), 1.82 d (3H, CH ₃), 3.20 m (1H, CH), 3.42 s (2H, NH ₂), 5.35 m (2H, CH=CH),
(11p)	108(3)	930, 1630, 3380. 3450	(4H, AF) $(1,17 d (3H, CH_3), 1.55 d (3H, CH_3), 2.12 s (3H, CH_3), 3.25 m (3H, NH_2, CH), 5,30 m (2H, CH= 0.01)$
(111b)	140(3)	980, 1610, 3355, 3425	= CH), $6.23-6.60$ qu (2H, Ar), $6.67 \le (1H. Ar)$ $1,25 \le (3H, CH_3), 1,62 \le (3H, CH_3), 3.12 \le (2H, NH_2), 3.30, m (1H. CH), 3.58 \le (3H, OCH_3),$ 5,40 m (2H, CH=CH), 6,30-6,62 qu (2H, Ar),
(IVb)	164(12)	980, 1625, 3380, 3450	6,38 s (1H, Ar) 1,25 d (3H, CH ₃), 1,61 d (3H, CH ₃), 2,67 m (1H, CH), 3,25 br.s (2H, NH ₂), 5,38 m (2H, CH=
(VÞ)	115-117(3)	980, 1620, 3360	CH), $6,50-7.00$ qu (2H, Ar), $6,90$ s(1H, Ar) 1,20 d (3H, CH ₃), 1,57 d (3H, CH ₃), 2,62 s (3H, CH ₃), 3,17 m (1H, CH), 3,59 s(1H, NH), 5,37 m
(VIb)	95(1)	980, 1610, 3400	(2H, CH=CH), $6,53-6,94$ m (4H, Ar) 1.07 t (3H, CH ₃), 1.22 d (3H, CH ₃), 1.53 d (3H, CH ₃), 2.94 qu (2H, CH ₂), 3.22 m (1H, CH), 3.54 s (1H, NH), 5.36 m (2H, CH=CH), 6.50-6.90 m
(VIIb)	148-150(8)	975, 1610, 2880, 3410	(4H. Ar) 1.05 t (3H, CH ₃), 1.33 d (3H, CH ₃), 1.68 m (5H, CH ₂ , CH ₃), 2.83-3.25 m (3H, CH, CH ₂ -N). 3.57 s (1H, NH), 5.45 m (2H, CH=CH), 6.35-
(VIIIb)	114-116(1)	980. 1370, 1390, 1600. 3400	-6.98 m (4H, Ar) 1.20 d (6H, 2CH ₃), 1.35 d (3H, CH ₃), 1.68 d (3H, CH ₃) 3,17-3.82 m (3H, 2CH, NH), 5,48 m (2H, CH=CH) 650-708 m (4H Ar)
(IX b)	126-129(3)	980. 1600, 2890, 3440	$(4H, CH, CH_3), 2,75-3,25 m (3H, CH_3), 1,58-1,78 m (4H, CH, CH_3), 2,75-3,25 m (3H, CH, CH_2), 3,73 br.s (1H, NH), 5,48 m (2H, CH=CH), (3H, CH=CH$
(Xb)	120-122(2)	980. 1370, 1400, 1605, 3420	6,42-7,10 m (4H, Ar) $1,35 \text{ s}$ (9H, 3CH_3), $1,35 \text{ d}$ (3H, CH_3), 1.63 d (3H, CH_3), $3,38 \text{ m}$ (1H, CH), $3,72 \text{ br.s}$ (1H, NH), 560-740 cm (1H, NH),
(X1b)	170-174(1)	990. 1520, 1605, 2940. 3425	3,30m (2H, CH=CH), $0.52-7,17$ m (4H, Ar) 1,33d (3H, CH ₃), 4.60d (3H, CH ₃), 3,30m (1H, CH), 3.83 s (1H, NH), 4,20 s (2H, CH ₂), 5,40 m (2H, CH=CH), 6,42-7,25 m (9H, 2Ar)

starting aniline), then cooled, ether was added, and the precipitated salt was filtered off. The ether and excess aniline were distilled from the filtrate, and the sediment was vacuum distilled to separate the final product.

The compounds synthesized were identified with the data from elementary analysis and the IR and ¹H NMR spectra (Table 1). The IR spectra were recorded on a UR-20 spectrometer (in a film), and the ¹H NMR spectra were recorded on a Tesla B-487 instrument in CCl₄ relative to TMS.

The kinetic experiments were conducted in sealed glass ampuls (\sim 1 ml volume of reaction mixture) placed in a thermostat. Freshly distilled nitrobenzene was used as the solvent. The HCl catalyst was added to the reaction system in hydrochlorides (Ia)-(XIa). The concentration of HCl in the starting solution was determined by titration with a 0.02 M alcohol solution of KOH in the presence of bromothymol blue. After a certain time the ampuls were removed from the thermostat, cooled to \sim 20°C, and opened. The reaction mixture was passed through a 180 × 4 mm column packed with freshly calcined K₂CO₃, washed with a small amount of alcohol, and analyzed by GLC for the concentration of substrate (A), product of rearrangement, and corresponding aniline, the product of elimination (internal standards: dodecane, pentadecane, and hexadecane). The analysis was conducted on a Khrom-5 chromatograph with a flame-ionization detector. Column 1 [analysis of compounds except for (IIa), (VIa)]: 3700 × 3 mm with 5% SE-30 on Chromaton N-AW-DMCS; column II [analysis of compounds (IIa) and (VIa)]: 2500 × 3 mm with 5% Carbowax-6000 on Inerton AW. Evaporator temperature 320°C, column temperature 170°C, and carrier gas (He) flow rate of 38 ml/min.

RESULTS AND DISCUSSION

The kinetic features of the HCl-catalyzed reaction of (Ia)-(IVa) were studied at 130°C. The presence of substituents at the nitrogen atom results in a sharp increase in the reaction rate; for this reason, the measurements were conducted at a lower temperature (110°C) for (Ia) and (Va)-(XIa). The first-order rate constants of rearrangement k_1 and elimination k_2 were determined from the starting rates of accumulation of the corresponding products similar to [1]. The dependence of k_1 and k_2 on the nature of R^1 and R^2 is reported in Table 2.

Rupture of the N-C bond takes place during rearrangement and elimination, and the amino group must consequently be considered the reaction site. For this reason, the Taft equation was used for describing the effects of substituents R^1 on the reactivity of (A), and modifications of the Hammett equation (the constants for the substituent were taken from [6]) were used for substituents R^2 .

As a result of the analysis of the kinetic data reported in Table 2, it was found that the effect of the nature of R^1 on rate constants k_1 and k_2 is described within the framework of two-parameter Taft equations

$$\lg k_i = \lg k_0 + \rho^* \sigma^* + \delta E_s \tag{1}$$

The following values of the reaction constants were obtained:

for rearrangement

$$\rho_1^* = 1.86 \pm 0.26, \ \delta_1 = -1.66 \pm 0.08, \ r = 0.998$$
 (1a)

for elimination

$$\rho_2^* = 0.12 \pm 0.48, \ \delta_2 = -0.71 \pm 0.17, \ r = 0.990$$
 (1b)

It follows from Eqs. (la) and (lb) that

$$lg (k_{i1}/k_{i2}) = 0.51 \pm (1.74 \pm 0.74) \,\sigma^* - (0.95 \pm 0.25) E_s \tag{2}$$

Here k_{11} and k_{12} are the rate constants of rearrangement and elimination of (a), which contains substituent $R^1 \neq Me$; k_{01} , k_{02} are the corresponding rate constants for methyl derivative (Va).

Equation (2) reflects the effect of the substituent at the nitrogen atom (R^1) on the selectivity of the process.

The dependence of k_2 on the nature of substituent R^2 can be described based on the following one-parameter equation (Fig. 1)

$$\lg k_{i2} = \lg k_{02} + (1.29 \pm 0.29) \sigma_{0}^{-1}$$

121

TABLE 2. Effect of the Structure of $4-R^2-N-R^1-N-(1-Methy)-2-buteny$ butenyl)aniline on the Rate Constants of Rearrangement k_1 and Elimination k_2 ([A]:[HC1] = 1:1; nitrobenzene)

() amo a con d		·	k₁-104	k ₂ -10*	
Compound	R'	R ²	sec ⁻¹		
		130°			
(Ia) (IIa) (IIIa) (IVa)	H H H H	H Me MeO Cl	$ \begin{array}{c c} 1.16 \pm 0.02 \\ 1.00 \pm 0.10 \\ 0.35 \pm 0.05 \\ 0.36 \pm 0.05 \end{array} $	$\begin{array}{c} 0.85 \pm 0.09 \\ 0.20 \pm 0.02 \\ 0.06 \pm 0.006 \\ 0.94 \pm 0.14 \end{array}$	
		110°			
(Ia) (Va) (VIa) (VIIa) (VIIIa) (IXa) (XIa)	H Me Et Pr <i>i</i> -Pr <i>i</i> -Bu PbCH ₂	H H H H H H H	$\begin{array}{c} 0.36 \pm 0.04 \\ 4.14 \pm 0.19 \\ 3.62 \pm 0.17 \\ 9.50 \pm 1.50 \\ 15.70 \pm 0.65 \\ 98.40 \pm 11.80 \\ 49.30 \pm 3.20 \end{array}$	$\begin{array}{c} 0.11 \pm 0.01 \\ 0.93 \pm 0.07 \\ 0.66 \pm 0.04 \\ 2.10 \pm 0.12 \\ 2.00 \pm 0.12 \\ 2.48 \pm 0.26 \\ 1.90 \pm 0.20 \end{array}$	

where σ_n^- are the nucleophilic constants of the substituents recommended for reactions of splitting from aniline ions [6, 7].

The attempt to describe rearrangement with an analogous equation was unsuccessful. Satisfactory results were obtained in using the two-parameter equation in [7], which simultaneously takes into consideration the change in the electron density on two reaction sites: on the nitrogen atom and in position 2 of the aromatic nucleus (see Fig. 1)

$$\lg k_{i1} = \lg k_{01} + \rho_1 \sigma_n^- + \rho_1^n \sigma_m^n$$
 (4)

According to the data in Fig. 1, $\rho_1^- = 0.48 \pm 0.09$; $\rho_1^n = -1.52 \pm 0.21$.

The dependence which reflects the effect of the nature of R^2 on the selectivity of the process derives from Eqs. (3) and (4)

$$lg (k_{i1}/k_{i2}) = 0.14 - (0.81 \pm 0.38) \sigma_n^{-} - (1.52 \pm 0.21) \sigma_m^{-}$$
(5)

It follows from Eq. (2) that the compounds with electron-acceptor substituents at the nitrogen atom, which have significant steric effects, form products of rearrangement more selectively; in addition, they also have higher rates of conversion. Substituents in position 4 of the aromatic nucleus have the opposite effect [Eq. (5)]: electron-donor substituents result in an increase in the selectivity of rearrangement, but also a decrease in the conversion rate (A), while electron-acceptor substituents cause an increase in the rate but decrease the selectivity of rearrangement.

The kinetic results are satisfactorily explained by the following mechanism (the Cl⁻ counterion is not shown in the scheme for simplicity)



According to this scheme, rupture of the N-C bond and formation of a molecular-ion complex (MIC) consisting of the mesomeric 1-methyl-2-butenyl cation and a molecule of an aromatic amine take place in the first stage of the process. The MIC formed is subsequently consumed in two separate directions. One is the reaction of the aromatic ring with the allyl cation, resulting in the formation of a σ complex [8, 9] which is stabilized by splitting of a proton. In the absence of more basic molecules in the reaction system, the proton is added to the



Fig. 1. Dependence of $(1/\sigma_n^-) \log (k_{11}/k_{o1})$ on σ_m^n/σ_n^- (1) and log (k_{12}/k_{o2}) on σ_n^- (2) (130°C, solvent: nitrobenzene; the numeration of the compounds corresponds to Table 2).

amino group of the product of rearrangement. The other direction of the process is decomposition of the MIC with exit of the allyl cation from the cage of the solvent, which requires additional expenditure of energy of up to 10 kcal/mole [10]. Splitting of a proton from the allyl cation and its addition to the molecule of the aromatic amine subsequently take place, and 1,3-pentadiene and a protonated aromatic amine are formed as a result.

The presence of the R¹ substituent at the nitrogen atom results in the formation of a "looser" MIC with a significant distance between fragments, which decreases the sensitivity of the stage of exit of the allyl cation from the solvent cage to the effects of the substituent ($\rho_2^* = 0.12 \pm 0.48$). In the stage of formation of the σ complex, the electrophilic attack of the aromatic nucleus takes place in the immediate proximity of the amino group, and for this reason the inhibiting effect of substituents R² is more strongly manifested ($\rho_1^* > \rho_2^*$). This could be the cause of the relatively high regioselectivity of Claisen amino rearrangement [8]. The accelerating effect of the steric effect of substituents R¹ is apparently caused by their shielding of the electrostatic effect of the amino group on the allyl cation ($\delta_1 < 0$, $\delta_2 < 0$). The electron-donor substituents R² also have an inhibiting effect on both reactions ($\rho_1^- > 0$, $\rho_2^- > 0$). However, in this case $\rho_2^- > \rho_1^-$, which could be caused by the closer position of the fragments in the MIC in the absence of bulky R¹ substituents at the nitrogen atom.

The relatively high value of ρ_1^n suggests a later transition state in the stage of formation of the σ complex, which usually arises on attack of the aromatic nucleus by a more selective electrophile [9] to which the allyl cation which has a significant delocalized positive charge can be assigned. The results obtained permit explaining the mechanism of acidcatalyzed Claisen amino rearrangement within the framework of the classic theory of electrophilic substitution in the aromatic series.

LITERATURE CITED

- 1. I. B. Abdrakhmanov, V. M. Sharafutdinov, N. G. Nigmatullin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1273 (1983).
- 2. S. Jolidon and H. J. Hansen, Helv. Chim. Acta, 60, 978 (1977).
- 3. S. Jolidon and H. J. Hansen, Chimia, <u>30</u>, 21 (1976).
- C. Weygand and G. Hilgetag (eds.), Organisch-chemische Experimentierkunst, 3rd ed., Barth, Leipzig (1964).
- 5. I. B. Abdrakhmanov, V. M. Sharafutdinov, U. M. Dzhemilev, et al., Zh. Prikl. Khim., 2121 (1982).
- E. T. Denisov, Kinetics of Homogeneous Chemical Reactions, Vyssh. Shkola, Moscow (1978), p. 135.
- Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry, Izd. Rost. Univ. (1966), pp. 106, 232.
- H. Becker, Einfuehrung in die Elektronentheorie organisch-chemischer Reaktionen, VEB Deutscher Verlag der Wissenschaften, Berlin (1961).

- 9. F. Keri and R. Sandberg, Advanced Course in Organic Chemistry [Russian translation], Khimiya, Moscow (1981), p. 355.
- 10. D. Bethell and V. Gold, Carbonium Ions, Academic Press, New York (1967).

ADDITION OF tert-PERFLUOROALKYL BROMIDES AT A MULTIPLE BOND,

INITIATED BY ELECTRON TRANSFER

S. M. Igumnov, I. N. Rozhkov, S. I. Pletnev, Yu. A. Borisov, and G. D. Rempel' UDC 542.955:547.412

The thermodynamics of the dissociation of the radical-anions of perfluoroalkyl halides was determined by quantum-chemical methods. The conditions for the addition of tertiary perfluoroalkyl bromides to alkenes, initiated by electron transfer, were obtained.

At the present time it has only been possible in practice to introduce perfluoroalkyliodides R_FI into the perfluoroalkylation under the conditions of homolytic addition of R_FI to alkenes and alkynes [1]. The substitution of iodine by a nucleophilic fragment [2-4] and radical-chain reactions, initiated by electron donors or transition metal complexes [5, 6], are also known for primary and secondary perfluoroalkyl iodides. Electron transfer from the donor to the R_FI molecule was postulated for the first stage of these reactions with the formation of an intermediate radical-anion, which then dissociates, giving a perfluoroalkyl radical capable of attacking the multiple bond (addition) or nucleophilic particle (S_{RN} l substitution):

$$R_F - I + e \rightarrow R_F - I^{-} \rightarrow R_F + I^{-}$$

However, as found, reactions of the $S_{\rm RN}$ l type are not realized for tertiary perfluoroalkyl iodides [7]. Only deiodofluorination by the action of the nucleophiles was observed for the compounds, and this was explained by halogenophilic attack by the nucleophile on the iodine atom of the perfluoroalkyl iodide. The proposed scheme seems to us unlikely, since it does not correlate with the stronger oxidizing power of tertiary perfluoroalkyl halides compared with secondary and, especially, primary halides.

RESULTS AND DISCUSSION

We supposed that the initial event in the reaction of tert-perfluoroalkyl iodides with soft nucleophiles and other electron donors is the formation of the radical-anion t-RFI, which unlike the primary and secondary radical-anions RFI dissociates into the tertiary perfluoro-carbanion and atomic iodine. This hinders the use of t-RFI in perfluoroalkylation initiated by electron transfer. We also supposed that the direction of the dissociation of the radical-anion RFX in the general case depends on the structure of RF, the nature of the halogen X, and the dielectric characteristics of the medium.

In order to determine the thermodynamics of one or the other path for the dissociation of the radical-anions of perfluoroalkyl halides we undertook a quantum-chemical study of these processes by the semiempirical AM1 method [8]. For this purpose we calculated in terms of a unified method the heats of formation of the primary, secondary, and tertiary radical-anions of perfluoroalkyl halides, perfluoroalkyl radicals and perfluoroalkylcarbanions and also the heats of formation of the anions and halogen atoms in the Cl, Br, I series. On the basis of the calculations we determined the enthalpies ΔH of reactions (1) and (2) (Table 1):

$$R_{F} - X^{-} \longrightarrow R_{F} + X^{-}$$
(1)

$$\xrightarrow{\Delta H_{t}} R_{F} + X^{*}$$
(2)

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2308-2312, October, 1989. Original article submitted June 23, 1988.