

Electrophilic Amination of Methylbenzenes with the System $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. Effects of the Solvent, Crown Ether, and Substrate Structure*

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Abstract—Using mesitylene and *o*-xylene as examples, it was shown that the solvent nature strongly affects the conversion of methylbenzenes in electrophilic amination with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. Two-parameter correlations were found between the substrate conversion, on the one hand, and dielectric constant and number of heavy atoms in the solvent, on the other. A considerable solvent effect on the regioselectivity of amination of *o*-xylene was observed. The presence of 18-crown-6 weakly affects the ratio of isomeric amines, but the conversion of *o*-xylene sharply decreases. Solid aromatic substrates, such as durene and pentamethylbenzene can also be involved in electrophilic amination with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. On the basis of the experimental data and the results of quantum-chemical calculations, participation of a nitrenium intermediate in this reaction was postulated.

Direct electrophilic amination [3–11] is a promising method for preparation of aromatic amines. It is more advantageous than common multistep procedures for building up a $\text{C}_{\text{arom}}\text{-NR}_2$ fragment, which imply introduction of a temporary functional group or atom [12–14]. A convenient reagent for direct electrophilic amination is sodium azide which is used under conditions of acid catalysis [1, 2, 5]. Olah *et al.* [5] studied electrophilic amination of benzene and its derivatives with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. The best results were obtained when excess aromatic substrate was used as solvent. When the reaction was carried in hexane, the yield of aromatic amine was lower, while 1,2-dichloroethane and nitromethane were shown [5] to be inappropriate solvents because of strong complex formation with the catalytic system. According to our data [2], the amination of mesitylene with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ in hexane and 1,2-dichloroethane affords 2,4,6-trimethylaniline in moderate (40%) and high (86%) yield, respectively.

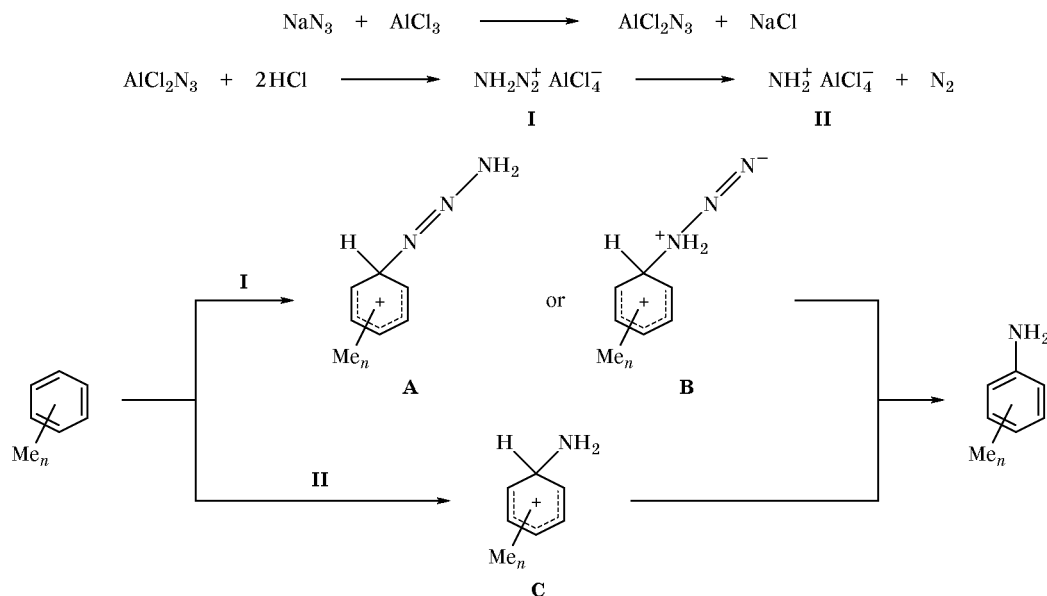
The goal of the present work was to examine the effects of substrate structure and solvent nature on

electrophilic amination of methylbenzenes with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. Scheme 1 shows the most probable mechanisms of this reaction (cf. [2, 5]).

According to Olah *et al.* [5], in the first stage sodium azide reacts with aluminum chloride; therefore, solvents capable of effectively coordinating to AlCl_3 should hinder the process. In fact, using mesitylene as substrate we found that solvents with a large donor number (greater than 2 according to Gutmann) [15], such as tetrahydrofuran, sulfolane, nitrobenzene, and nitromethane, afford low conversion of aromatic substrate (Table 1). Protonation of AlCl_2N_3 species gives diazonium ion **I** which loses nitrogen molecule to form nitrenium ion **II**. The reaction of methylbenzenes with ion **I** could give two different σ -complexes **A** and **B**. According to the results of AM1 quantum-chemical calculations, σ -complexes **A** are less stable than **B** (Fig. 1); therefore, the formation of complexes like **B** seems to be more energetically favorable. Complexes **B** are characterized by a very long $\text{H}_2\text{N-N}$ bond (~ 3 Å), and they resemble σ -complexes **C** in this respect. Complexes **C** could be formed by reaction of nitrenium ion **II** with methylbenzenes. It should be noted

* For preliminary communications, see [1, 2].

Scheme 1.



that the geometric parameters of σ -complexes **A**, **B**, and **C** within the corresponding series are similar; therefore, we can expect that reactions of methylbenzenes with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ follow a common mechanism.

According to published data [3], the ground state of the NH_2^+ cation is triplet ($^3\text{NH}_2^+$); its energy is lower by 125.9 kJ/mol than the energy of the singlet state ($^1\text{NH}_2^+$) [18]. Taking into account that the formation of σ -complexes **C** requires singlet state of the nitrenium ion, the substrate conversion should depend on the probability of singlet-triplet inversion of that cation. This probability should increase with increase in the number of heavy atoms in the solvent molecule and increase in their atomic number [3]. As follows from the data in Table 1, the conversion of mesitylene and *o*-xylene decreases in the series $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$, $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{ClCH}_2\text{CCl}_3$, and $\text{CH}_2\text{Cl}_2 > \text{CH}_2\text{Br}_2$. This is consistent with the assumed participation of NH_2^+ ion as reactive intermediate.

Presumably, the rate-determining stage is formation of σ -complex **C**. Taking into account its polar character, the conversion of methylbenzenes should depend not only on the number of heavy atoms (N) in the solvent molecule but also on the dielectric constant (ϵ). This follows from the existence of two-parameter correlations (1) and (2) for the reactions with mesitylene and *o*-xylene, respectively, where η is the mole fraction of 2,4,6-trimethylaniline or 2,3- and 3,4-dimethylanilines in the mixture with mesitylene or *o*-xylene, and N_{Cl} is the number of chlorine atoms in the solvent molecule.

$$\eta = (0.29 \pm 0.08) + (0.067 \pm 0.010)\epsilon - (0.107 \pm 0.023)N_{\text{Cl}}; \quad (1)$$

$$r = 0.97, s = 0.08, n = 9;$$

$$\eta = (0.40 \pm 0.10) + (0.059 \pm 0.012)\epsilon - (0.143 \pm 0.027)N_{\text{Cl}}; \quad (2)$$

$$r = 0.96, s = 0.1, n = 7.$$

Figures 2 and 3 show correlations between the experimental mole fractions of tri- and dimethylanilines and those calculated by Eqs. (1) and (2), respectively. A considerable contribution of the term including the dielectric constant ϵ (which characterizes the solvent polarity) is consistent with the assumed ionic reaction mechanism.

Singlet nitrenium ion $^1\text{NH}_2^+$ is likely to be a very strong electrophile; therefore, the regioselectivity in the amination of substituted benzenes with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ should be low. This aspect of the process was studied using *o*-xylene as substrate. The mole fractions of 2,3- and 3,4-dimethylanilines given in Table 1 indicate that the regioselectivity is in fact low. By varying the solvent, the ratio of 2,3- and 3,4-dimethylanilines can be changed from 0.56 to 0.90. Here, the fraction of 3,4-dimethylaniline is always greater than the fraction of 2,3-dimethylaniline. These data are in agreement with the results of AM1 quantum-chemical calculations, according to which σ -complex **C-2** is more stable than **C-1** (Fig. 1).

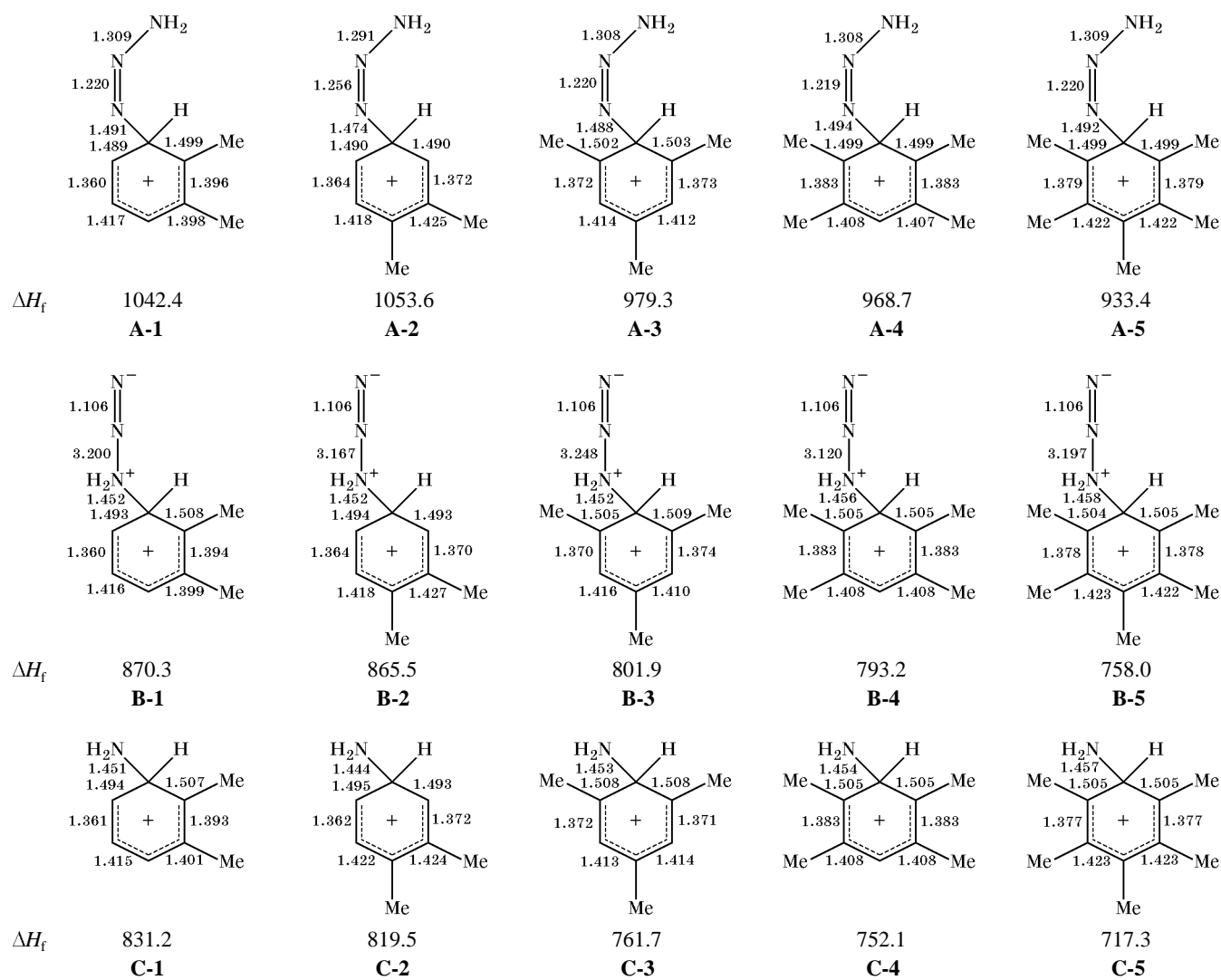


Fig. 1. Heats of formation ΔH_f (kJ/mol) of σ -complexes A–C and bond lengths (\AA) therein (AM1 calculation).

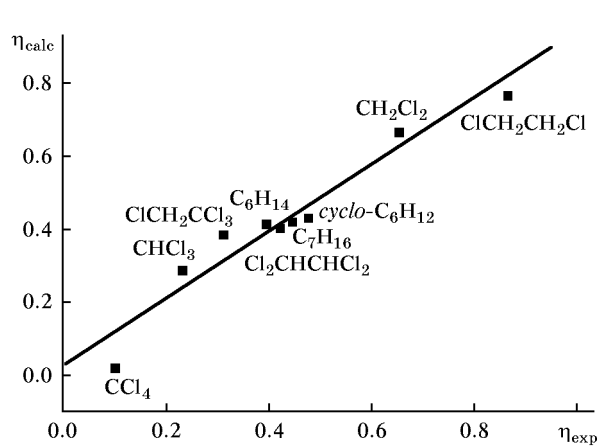


Fig. 2. Correlation between the calculated and experimental conversion of mesitylene in the amination with the system $\text{NaN}_3\text{--AlCl}_3\text{--HCl}$.

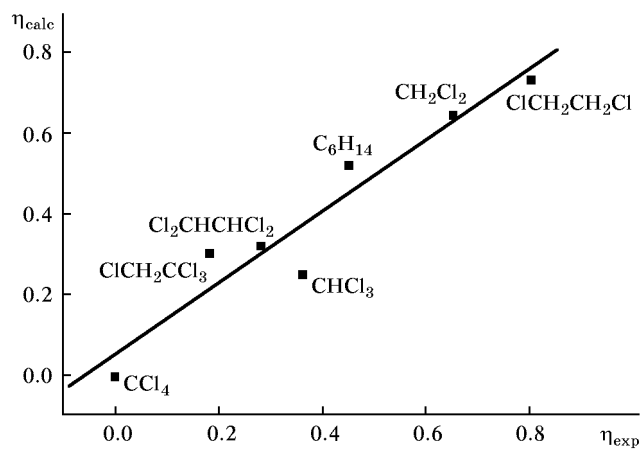


Fig. 3. Correlation between the calculated and experimental conversion of *o*-xylene in the amination with the system $\text{NaN}_3\text{--AlCl}_3\text{--HCl}$.

It was interesting to compare the regioselectivity observed in the amination of *o*-xylene and in other electrophilic substitution reactions with the same substrate (Table 2). It is seen that the regioselectivity in the amination of *o*-xylene changes to a lesser extent than in the nitration and bromination; in some cases, the isomer ratio is reversed. Presumably, this is the result of change of the reaction mechanism. In the nitration with the $\text{NO}_2^+ \text{BF}_4^-$ -sulfolane system, the fraction of 1-nitro-2,3-dimethylbenzene is larger than that of 1-nitro-3,4-dimethylbenzene, while in the nitration with $\text{HNO}_3\text{-H}_2\text{SO}_4$ (54%) and $\text{HNO}_3\text{-Ac}_2\text{O}$ the reverse situation is observed. It is known that nitronium tetrafluoroborate is a strong electrophile; therefore, the high regioselectivity but low substrate selectivity is explained by the fact that the rate-determining stage is formation of π -complex rather than σ -complex [21], as in the other nitration reactions.

The activity of a reagent in electrophilic aromatic substitution can be estimated from the Brown-Stock relation between the substrate selectivity and regioselectivity [30]. Santiago and Houk [31] compared the substrate selectivities and regioselectivities for 108 electrophilic substitution reactions of toluene and obtained correlation (3):

$$\log f_p = -0.17 + 1.38 S_f; \quad r = 0.91. \quad (3)$$

Here, f_p is a factor characterizing partial rate of hydrogen substitution in the *para* position of toluene, and S_f is a selectivity factor which is equal to the ratio f_p/f_m for toluene. The correlation was improved by exclusion of the data for nitration of toluene with $\text{NO}_2^+ \text{BF}_4^-$ in polar aprotic solvents and some other data (total of 8 points); as a result, correlation (4) was obtained [31]:

$$\log f_p = -0.08 + 1.37 S_f; \quad r = 0.95. \quad (4)$$

Calculation by Eqs. (3) and (4) of $\log f_p$ for amination of toluene with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ [5] gives values of 0.87 and 0.95, respectively, which approach the experimental value (0.97). The low values of $\log f_p$ and S_f for the reaction under study (0.97 and 0.75, respectively) suggest that the nitronium ion is a very active intermediate species whose reactivity is comparable to those observed in the alkylation with MeBr-GaBr_3 , EtBr-GaBr_3 , and $i\text{-PrBr-GaBr}_3$ (the parameters $\log f_p$ and S_f are equal to 1.072 and 0.842, 0.780 and 0.587, and 0.703 and 0.554, respectively [32]). In the alkylation of *o*-xylene

Table 1. Conversions of mesitylene and *o*-xylene (η)^a in the amination with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ and solvent parameters (ϵ , DN)

Solvent	ϵ [16]	DN [15]	η	
			TMA ^b	DMA ^c
Hexane	1.89	~0	0.40	0.45 (0.80)
Heptane	1.92	~0	0.44	
Cyclohexane	2.02	~0	0.47	
CHCl_3	4.70	–	0.23	0.36 (0.83)
CH_2Cl_2	8.9	–	0.65	0.65 (0.67)
CCl_4	2.23	~0	0.10	0
$\text{ClCH}_2\text{CH}_2\text{Cl}$	10.4	0.1	0.86	0.80 (0.68)
$\text{Cl}_2\text{CHCHCl}_2$	8.2	–	0.42	0.28 (0.90)
$\text{ClCH}_2\text{CCl}_3$	7.93 ^d	–	0.31	0.18 ^e
CH_2Br_2	6.7	–	0.44	0.48 (0.56)
C_6F_6			0.17	
THF	7.32	20.0	<0.04	
PhNO_2	35	4.4	<0.04	
Sulfolane	44	14.8	~0	
$\text{CH}_2\text{Cl}_2\text{-MeNO}_2$ (1:1, v/v)	38.6 ^f	2.7 ^f	~0.02	

^a η stands for the mole fraction of 2,4,6-trimethylaniline or dimethylaniline, taking into account that 2 equiv of the aromatic substrate was involved with respect to NaN_3 ; $\eta = 2x/(x+y)$, where x and y are the mole fractions of ArNH_2 and ArH , respectively. Given are averaged values determined from the ¹H NMR and GC-MS data.

^b 2,4,6-Trimethylaniline.

^c 2,3- and 2,4-Dimethylanilines; their molar ratio is given in parentheses.

^d At -40°C [17].

^e The ratio of 2,3- and 3,4-dimethylanilines was not determined, for the ¹H NMR spectrum contained foreign signals.

^f Parameters of MeNO_2 .

with $\text{PrOH-H}_2\text{SO}_4$, where the reactive intermediate is assumed to be isopropyl cation (as in the alkylation $i\text{-PrBr-GaBr}_3$), the ratio of 1-isopropyl-2,3-dimethylbenzene to 1-isopropyl-3,4-dimethylbenzene is considerably smaller than unity (Table 2). Reduction of this ratio in going from amination to alkylation may be due to greater steric hindrance to electrophilic attack by Me_2CH^+ , as compared to NH_2^+ .

The effective size of NH_2^+ ion can be increased, e.g., via complex formation with crown ethers. The results of AM1 quantum-chemical calculations showed that the cavity of 18-crown-6 readily accommodates NH_2^+ ion (Fig. 4), thus forming a quite stable complex ($\Delta\Delta H_f = 296.6$ kJ/mol). However, addition

Table 2. Isomer ratios of 1-X-2,3-dimethyl- (A) and 1-X-3,4-dimethylbenzenes (B) in electrophilic substitution in *o*-xylene

X	Electrophilic system	Temperature, °C	Molar ratio A:B	Reference
NO ₂	HNO ₃ -54% H ₂ SO ₄ ^a	25	0.50	[19]
	90% HNO ₃ -98% H ₂ SO ₄	0	1.56	[20]
	HNO ₃ -Ac ₂ O ^a	25	0.54	[19]
	NO ₂ ⁺ BF ₄ ⁻ -sulfolane	25	3.93	[21]
NO	NO-CF ₃ COOH	38	0.61 ^b	[22]
	Cl ₂ -AlCl ₃ -MeNO ₂ - <i>o</i> -xylene	25	0.78	[23]
	Cl ₂ -FeCl ₃ -MeNO ₂	25	0.78	[23]
	Cl ₂ -FeCl ₃ - <i>o</i> -xylene	25	0.70	[23]
Br	Br ₂ -FeCl ₃ -MeNO ₂	25	2.13	[24]
	Br ₂ -AcOH	25	0.41	[25]
	Br ₂ -AcOH-H ₂ O	25	0.33	[25]
	Br ₂ -CF ₃ COOH	25	0.14	[26]
	Br ₂ -SO ₂	-9	0.07	[26]
	Br ₂ -ClCH ₂ CH ₂ Cl	20	0.18	[26]
	Br ₂ -Ti(OCOMe) ₃ -CCl ₄	- ^c	≤0.18	[27]
	HBrO-AcOH	25	0.72	[25]
<i>i</i> -Pr	PrOH-80% H ₂ SO ₄	70-80	0.15-0.19	[28]
	<i>i</i> -PrOH-80% H ₂ SO ₄	70-80	0.15-0.19	[28]
2-Bu	BuOH-85% H ₂ SO ₄	25-30	~0.1	[28]
	2-BuOH-80% H ₂ SO ₄	70-80	~0.1	[28]
<i>t</i> -Bu	<i>t</i> -BuOH-80% H ₂ SO ₄	70-80	0.01-0.02	[28]
	<i>i</i> -BuOH-80% H ₂ SO ₄	70-80	0.01-0.02	[28]
	2-Methylbutene-AlCl ₃ -MeNO ₂	25	0	[29]
	<i>t</i> -BuBr-SnCl ₄ -MeNO ₂	25	0	[29]

^a The concentration of HNO₃ was not given.

^b Calculated from the kinetic data.

^c Heating in boiling carbon tetrachloride.

of even small amounts of 18-crown-6 to the aminating system sharply reduces the conversion of *o*-xylene, while the regioselectivity changes only slightly (Table 3). Presumably, the conversion decreases as a result of reduction of the acidity of the medium, which hampers formation of reactive intermediate according to Scheme 1. Binding of NH₂⁺ ion into a complex with crown ether is unlikely to be the reason for its reduced reactivity since the positive charge on the nitrogen changes insignificantly, from 0.489 to 0.428. It should be noted that, by contrast, addition of 18-crown-6 to the system benzene-CF₃COOH (which is obviously characterized by lower acidity than the system NaN₃-AlCl₃-HCl) in the photochemical generation of NH₂⁺ from 1-aminopyridinium or 1-aminoquinolinium salts increases the yield of aniline [33].

According to the results of our experimental study of the amination of mesitylene and *o*-xylene, the maximal yield of aminoarenes is achieved in such solvents as CH₂Cl₂ and ClCH₂CH₂Cl. We anticipated that the use of these solvents will allow us to involve in electrophilic amination solid substrates (under normal conditions) and obtain the corresponding arylamines in a sufficiently high yield. It should be emphasized that Olah and co-workers [5] used excess liquid aromatic substrate and that solid arenes have not been brought so far into electrophilic amination with the system NaN₃-AlCl₃-HCl [1, 2, 5]. We performed electrophilic amination of durene and pentamethylbenzene (which are solid substances at the reaction temperature) in one of the above solvents. As in the reactions with mesitylene and *o*-xylene, from durene in methylene chloride we obtained the

corresponding monoamination product, 2,3,5,6-tetramethylaniline, in 30% yield. The yield of pentamethylaniline was appreciably larger (52%).

Thus, using polymethylbenzenes as examples, we have demonstrated a strong effect of the solvent on the substrate conversion and regioselectivity of electrophilic amination with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. The use of such solvents as methylene chloride and 1,2-dichloroethane makes it possible to involve in this reaction aromatic compounds which are solid substances under standard conditions.

EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker WP-200-SY, AC-200, and AM-400 spectrometers in CDCl_3 using the solvent (δ 7.24 ppm) and HMDS (δ 0.04 ppm) as internal references. Gas chromatographic–mass spectrometric data were obtained on a Hewlett Packard G1800A setup consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector; energy of ionizing electrons 70 eV; oven temperature programming from 50°C (2 min) to 280°C at a rate of 10 deg/min; injector temperature 280°C; ion source temperature 173°C; 30-mm \times 0.25-mm HP-5MB capillary column (5% of diphenylsiloxane and 95% of dimethylsiloxane, film thickness 0.25 μm); carrier gas helium, flow rate 1 ml/min. Quantitative analysis of the reaction mixtures was performed by the internal normalization technique. AM1 quantum-chemical calculations [34] were performed with the aid of HyperChem 5.02 software with full geometry optimization of the cations.

Sodium azide of pure grade was dried over P_2O_5 under reduced pressure; aluminum chloride of pure grade (Merck) was sublimed under reduced pressure; reagent-grade *o*-xylene and mesitylene were distilled over molecular sieves; durene, pentamethylbenzene, and 2,3-dimethylaniline (all of pure grade) were distilled. 18-Crown-6 was synthesized at the pilot factory at the Novosibirsk Institute of Organic Chemistry and was dried over P_2O_5 . Hydrogen chloride was prepared by the procedure described in [35] and was dried by passing through concentrated sulfuric acid and a column charged with P_2O_5 . The solvents: CH_2Cl_2 , CH_2Br_2 [36], hexane, heptane, cyclohexane, 1,2-dichloroethane, CHCl_3 , CCl_4 , PhNO_2 , sulfolane [16], MeNO_2 , and $\text{Cl}_2\text{CHCHCl}_2$ [37] were purified by standard procedures. 1,1,1,2-Tetrachloroethane was synthesized and purified as described in [17]. Tetrahydrofuran of pure grade was distilled over metallic sodium. Hexafluorobenzene (pure) was dried over molecular sieves.

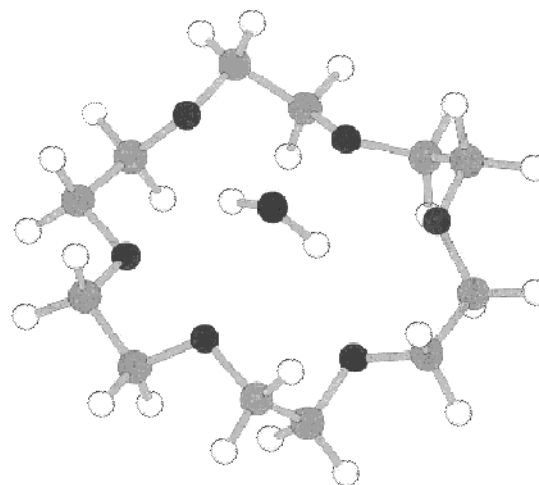


Fig. 4. Structure of the complex of 18-crown-6 with NH_4^+ ion, optimized by the AM1 method.

Amination of methylbenzenes (general procedure). A mixture of 3.65 mmol of sodium azide and 3.65 mmol of anhydrous aluminum chloride in 3.5 ml of appropriate dry solvent was stirred for ~20 h at room temperature. Methylbenzene, 7.3 mmol, was added, and dry hydrogen chloride was passed through the mixture at 20–25°C over a period of 2 h (until nitrogen no longer evolved). The mixture was poured onto ice, treated with excess concentrated aqueous sodium hydroxide, and extracted with diethyl ether (3 \times 15 ml). The extract was dried over MgSO_4 , and the solvent was distilled off.

In experiments with crown ether, 18-crown-6 was added to the system in an amount specified in Table 3 (with respect to sodium azide) before passing HCl. Methylene chloride was used as solvent.

The composition of the amination products was determined from the ^1H NMR and GC–MS data. The

Table 3. Effect of 18-crown-6 on the isomer ratio of 2,3- (**A**) and 3,4-dimethylanilines (**B**) and on the substrate conversion (η) in the amination of *o*-xylene with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ in CH_2Cl_2 (20°C)

Ratio 18-crown-6– NaN_3^a	Ratio A : B ^{a,b}	η
0	0.67	0.65
0.05	0.59	0.65
0.1	0.61	0.54
0.5	– ^c	<0.02

^a Molar ratio.

^b Determined from the GC–MS data.

^c The conversion of toluene was very low.

amination products of *o*-xylene were identified by comparison with authentic samples which were prepared by the procedure reported in [5] and purified by thin-layer chromatography on Al₂O₃. The structure of 2,3-dimethyl- and 3,4-dimethylanilines was determined by ¹H NMR spectroscopy using an available authentic sample of 2,3-dimethylaniline.

The results of the amination of *o*-xylene with the system NaN₃–AlCl₃–HCl in CH₂Cl₂ were checked for reproducibility. The mean deviation in the GC–MS determination of 2,3- and 3,4-dimethylanilines was ±0.1%. The mean deviation in the determination of the conversion of mesitylene (in hexane, heptane, CH₂Cl₂, CHCl₃, CCl₄, ClCH₂CH₂Cl, and ClCH₂CH₃) by ¹H NMR and GC–MS was ±13%.

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