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**SHORT
COMMUNICATIONS**

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Lewis Acid Effects in Mesitylene Amination in the System NaN$_3$–MHlg$_n$–HCl

I. Borodkin[1,2], A.A. Bessonov[1,2], R.V. Andreev[1], and V.G. Shubin[1]

[1]*Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Divisoion, Russian Academy of Sciences
Novosibirsk, 630090 Russia
e-mail: gibor@nioch.nsc.ru*
[2]*Novosibirsk State University Novosibirsk, 630090 Russia*

In recent year an interest grew to direct electrophilic amination of arenas (see [1–13] and references therein). One among promising reagents for this reaction is sodium azide under conditions of acid catalysis [11–13]. These studies were applied to electrophilic amination of benzene and its derivatives in a system NaN$_3$–AlCl$_3$–HCl. The best results were obtained at the use as solvent of the excess aromatic substrate [11] or dichloroethane [12, 13]. Only AlCl$_3$ served as Lewis acid [11–13].

The goal of this study was an attempt to involve other Lewis acids into this reaction and to find the media most suitable thereto. The effect of Lewis acid in electrophilic amination of arenas with the use of system NaN$_3$–MHlg$_n$–HCl was studied by an example of mesitylene in dichloroethane as solvent.

We established that mesitylene conversion strongly depended on the Lewis acid nature. At application of acids like TiCl$_4$ and SnCl$_4$ the conversion was very low, and GeCl$_4$ and SbCl$_3$ were quite useless for amination (see table). Acids SbCl$_5$, FeCl$_3$, and AlBr$_3$ are moderately active, and the most suitable for amination proved to be GaCl$_3$, ZrCl$_4$, and AlCl$_3$.

The most probable reaction mechanism is presented on the scheme (cf. [11–13]).

According to the scheme the nature of the Lewis acid apparently should not notably affect the stages (3) and (4), but its influence would have been observed in the stages (1) and (2). In the first stage sodium azide interacts with the Lewis acid (cf. [11–13]) and therefore if the metal cation weakly interacts with N$_3^-$ anion the reaction would be hampered. The calculations by PM3 procedure revealed that enthalpy variations for stage (1) are very small (see table) save the reaction with AlBr$_3$

Mesitylene conversion in amination by a system NaN$_3$–MHlg$_n$–HCl, and enthalpy variation at stages (1) and (2) ($\Delta\Delta H_1$ and $\Delta\Delta H_2$ respectively) calculated by PM3[a] procedure

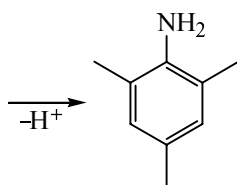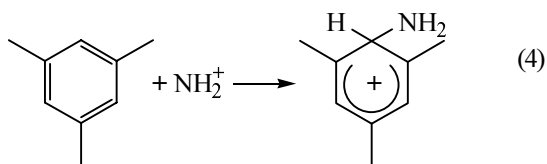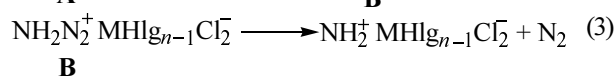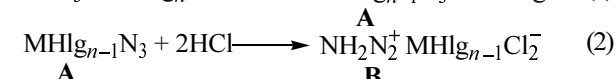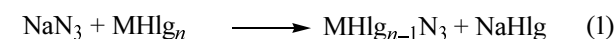| Lewis Acid	η[b]	$\Delta\Delta H_1$, kJ mol^{-1}	$\Delta\Delta H_2$, kJ mol^{-1}
GaCl$_3$	0.89 ± 0.07	–7.7	277.8
ZrCl$_4$	0.86 ± 0.08		
AlCl$_3$	0.86[c]	4.1	316.1
AlBr$_3$	0.68 ± 0.08	74.9	276.5
FeCl$_3$	0.61 ± 0.10		
SbCl$_5$	0.51 ± 0.07	–3.2	368.9
SnCl$_4$	0.009 ± 0.002[d]	11.3	364.9
TiCl$_4$	0.007 ± 0.003[d]		
SbCl$_3$	~0.001[d]	–6.8	391.4
GeCl$_4$	0	–5.8	447.6

[a] For some Lewis acids no calculations were performed for the parametrizations of the central atom was lacking.
[b] η is .the rlative molar fraction of mesidine with respect to NaN$_3$. Average η values are given obtained by ^{1}H NMR spectroscopy and GC-MS method for 2–3 runs.
[c] Data from [12, 13].
[d] GC-MS data.

that is the most exothermic. The protonation stage for intermediate MHlg$_{n-1}$N$_3$ (**A**) is endothermic and it apparently governs the relative reaction rates. This statement is supported by the observed trend in growing mesitylene conversion η with decresing $\Delta\Delta H_2$ values. The analysis based on the quantum-chemical calculations does

$$NaN_3 + MHlg_n \longrightarrow MHlg_{n-1}N_3 + NaHlg \quad (1)$$
$$\underset{\mathbf{A}}{}$$

$$\underset{\mathbf{A}}{MHlg_{n-1}N_3} + 2HCl \longrightarrow \underset{\mathbf{B}}{NH_2N_2^+ \, MHlg_{n-1}Cl_2^-} \quad (2)$$

$$\underset{\mathbf{B}}{NH_2N_2^+ \, MHlg_{n-1}Cl_2^-} \longrightarrow NH_2^+ \, MHlg_{n-1}Cl_2^- + N_2 \quad (3)$$

(4)

not take into account the solvent effects and the state of aggregation of the reactants and thus should be regarded as preliminary.

The activity series for Lewis acid we obtained ($GaCl_3 \sim ZrCl_4 \sim AlCl_3 > AlBr_3 > FeCl_3 > SbCl_5 \gg SnCl_4, TiCl_4 > SbCl_3, GeCl_4$) is unlike that observed for catalysts of Friedel–Crafts reaction ($Al_2Br_6 > Al_2Cl_6 > Ga_2Cl_6 > Fe_2Cl_6 > SbCl_5 > ZrCl_4, SnCl_4 > SbCl_3$) [14] (cf. [15]). A similar discrepancy in the data on Lewis acid activity is also observed for another process, addition of organosilicon ether to benzaldehyde and N-benzylideneaniline [16]. Thus according to classification given in [16], $SnCl_4$, $TiCl_4$, and $SbCl_3$ were very active acids whereas in arene amination with the system NaN_3–$MHlg_n$–HCl they are fairly inert.

The results obtained are consitent with existing observations that the activity of Lewis acids cannot be expressed by a unique series.

General procedure for mesitylene amination. A dispersion of dry NaN_3 (3.65 mmol) and anhydrous Lewis acid (3.65 mmol) in 4 mi of anhydrous $ClCH_2CH_2Cl$ was stirred for 20 h at room temperature. On adding mesitylene (7.3 mmol) into the reaction mixture was passed at stirring for 2 h dry hydrogen chloride at 20–25°C. Then the mixture was poured on ice, treated with excess concn. NaOH solution, extracted with Et_2O (3×15ml), dried on $MgSO_4$, and ether was distilled off. The products composition was analysed by ^1H NMR and GC–MS methods.

NMR spectra of solutions in $CDCl_3$ were registered on spectrometers Bruker AC-200 and WP-200-SY, internal references residual protons in $CDCl_3$ (δ_H 7.24 ppm)

and HMDS (δ_H 0.04 ppm.). GC–MS measurements were carried out on Hewlett Packard G1800A instrument including a gas chromatograph HP5890 and a mass-selective detector HP5971. Ionizing electrons energy 70 eV, oven heating mode as follows: 2 min at 50°C, then heating at a rate 10 deg/min till 280°C, column 30000×0.25 mm, stationary phase copolymer HP-5MB (5% of diphenyl-, 95% dimethulsiloxane), carrier gas helium, flow rate 1 ml/min. The quantitative analysis of mixtures was performed by internal normalization

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