

SHORT
COMMUNICATIONS

Solvent Effects in the Electrophilic Amination of Mesitylene with the System $\text{NaN}_3\text{--AlCl}_3\text{--HCl}$ *

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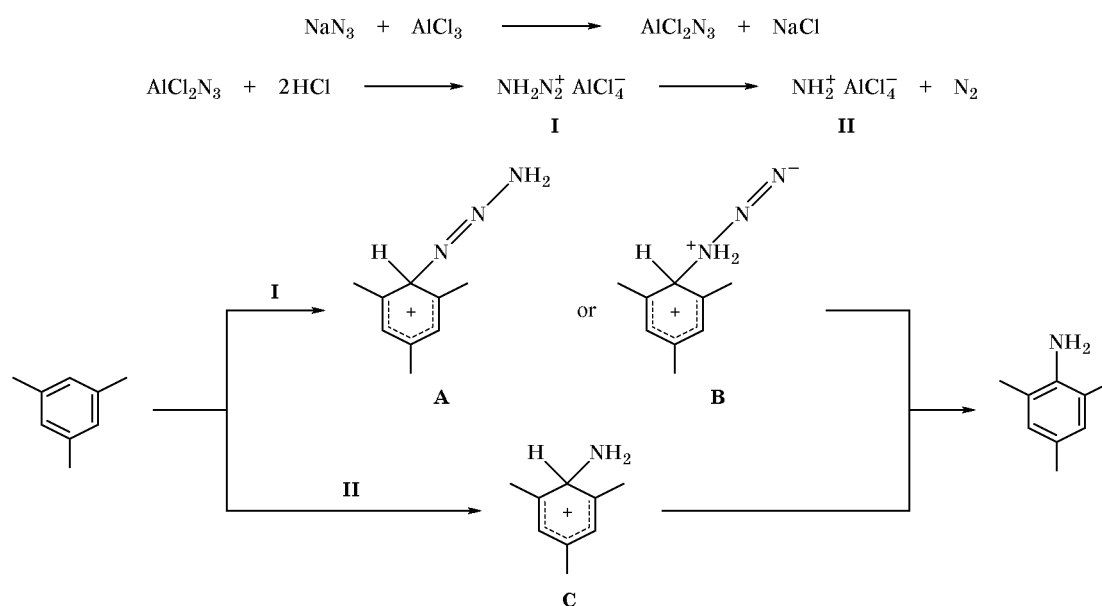
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Substitution of hydrogen in an aromatic ring by amino group is usually a two-step process which implies introduction of a temporary functional group or atom [2–4]. In the recent years, an interest has grown in direct electrophilic amination of arenes (see [5, 6] and references therein). A convenient reagent for direct electrophilic amination is sodium azide which is used under conditions of acid catalysis [7]. Olah *et al.* [7] 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 out in hexane, the yield of aromatic amine was lower, while 1,2-dichloroethane and nitromethane were shown [7] to be inappropriate solvents because of strong complex formation with the catalytic system.

The goal of the present work was to study solvent effect in the direct electrophilic amination of mesitylene with the system $\text{NaN}_3\text{--AlCl}_3\text{--HCl}$. The most probable mechanisms of this reaction are shown in Scheme 1 (cf. [7]). According to this scheme, in

Scheme 1.



* For preliminary communication, see [1].

Conversions of mesitylene (η)^a in the amination with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$ and solvent parameters (dielectric constants ϵ and donor numbers DN)

| Solvent | ϵ [10] | DN [8] | η |
|--|-------------------|------------------|--------|
| Hexane | 1.89 | ~0 | 0.40 |
| Heptane | 1.92 | ~0 | 0.44 |
| Cyclohexane | 2.02 | ~0 | 0.47 |
| CHCl_3 | 4.70 | – | 0.23 |
| CH_2Cl_2 | 8.9 | – | 0.65 |
| CCl_4 | 2.23 | ~0 | 0.10 |
| $\text{ClCH}_2\text{CH}_2\text{Cl}$ | 10.4 | 0.1 | 0.86 |
| $\text{Cl}_2\text{CHCHCl}_2$ | 8.2 | – | 0.42 |
| $\text{ClCH}_2\text{CCl}_3$ | 7.93 ^b | – | 0.31 |
| CH_2Br_2 | 6.7 | – | 0.44 |
| 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 ^c | 2.7 ^c | ~0.02 |

^a η stands for the mole fraction of 2,4,6-trimethylaniline relative to NaN_3 ; given are averaged values determined from the ^1H NMR and GC-MS data.

^b At -40°C [11].

^c Parameters of MeNO_2 are given.

the first stage sodium azide reacts with aluminum chloride; therefore, solvents capable of coordinating to AlCl_3 hamper the process. In fact, solvent with a large donor number ($\text{DN} > 2$, according to Gutmann [8]) ensure low conversion of mesitylene (see table). The reactive species may be diazonium (**I**) or nitrenium cation (**II**), and the reaction of the former with mesitylene could give two σ -complexes **A** and **B**.

According to AM1 quantum-chemical calculations, σ -complex **A** is less stable than isomeric σ -complex **B** ($\Delta H_f = 979.3$ and 801.9 kJ/mol, respectively); therefore, the formation of complex **B** is more favorable. σ -Complex **B** is characterized by a very long $\text{H}_2\text{N-N}_2$ bond (3.25 Å), so that it resembles σ -complex **C**. The latter is formed by reaction of nitrenium ion **II** with mesitylene. It is known that the ground state of NH_2^+ ion is triplet; its energy is by 125.9 kJ/mol lower than that of the singlet state [9]. Taking into account that the formation of σ -complex **C** requires singlet state of nitrenium ion, the conversion of mesitylene should depend on the probability for singlet-triplet inversion of the cation. This probability should increase with rise in the number of heavy atoms in solvent molecule and their atomic number [5]. The

data in table show that the conversion of mesitylene falls down in the series $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$, $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{Cl}_2\text{CHCHCl}_2$, and $\text{CH}_2\text{Cl}_2 > \text{CH}_2\text{Br}_2$, which are consistent with the assumption that NH_2^+ ion is the reactive intermediate species.

Apart of the number of heavy atoms N in solvent molecule, the conversion of mesitylene should depend on dielectric constant ϵ of the solvent. This follows from the existence of the two-parameter correlation

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

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

where η is the mole fraction of 2,4,6-trimethylaniline, and N_{Cl} is the number of chlorine atoms in solvent molecule. A considerable contribution of the term including ϵ , which characterizes solvent polarity, is consistent with the above presumed ionic mechanism.

General procedure for direct electrophilic amination of mesitylene with the system $\text{NaN}_3\text{-AlCl}_3\text{-HCl}$. A suspension of 3.65 mmol of dry sodium and 3.65 mmol of anhydrous AlCl_3 in 3.5 ml of appropriate dry solvent was stirred for ~20 h at room temperature. Mesitylene, 7.3 mmol, was added, and dry hydrogen chloride was passed through the mixture at $20\text{-}25^\circ\text{C}$ over a period of 2 h. The mixture was poured onto ice, treated with excess concentrated aqueous sodium hydroxide, and extracted with diethyl ether (3×15 ml). The extract was dried over MgSO_4 , and the solvent was distilled off. The product composition was determined by ^1H NMR spectroscopy and gas chromatography-mass spectrometry.

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