

SHORT
COMMUNICATIONSElectrophilic Amination of Methylbenzenes with Sodium Azide
in Trifluoromethanesulfonic Acid

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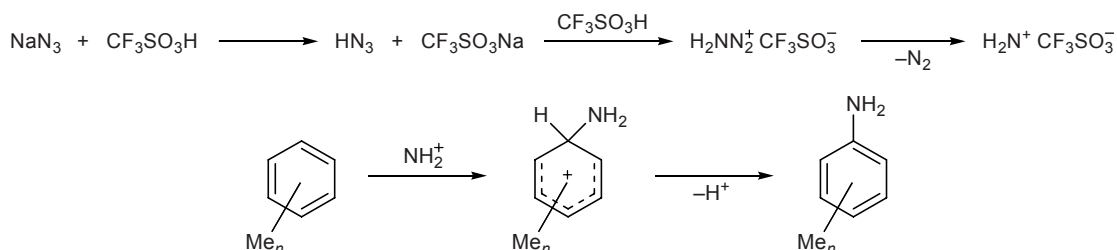
We previously found that the nature of solvent and Lewis acid strongly affects the yield of the amination products of methylbenzenes in the system $\text{NaN}_3\text{--MHlg}_n\text{--HCl}$ [1–4]. The most effective solvents were methylene chloride and 1,2-dichloroethane [1–3], as well as ionic liquids [4]. Takeuchi et al. [5] reported on electrophilic amination of arenes using hydrazoic acid and $\text{CF}_3\text{SO}_3\text{H--CF}_3\text{CO}_2\text{H--CHCl}_3$ mixture as solvent.

Ecological and economic aspects force chemists to minimize amount of solvent and even exclude it while carrying out chemical reactions [6]. The goal of the present work was to effect direct amination of arenes with the system sodium azide–trifluoromethanesulfonic acid using stoichiometric or nearly stoichiometric amounts of the reactants. We previously presumed [1–4] that the reactive species in electrophilic amination is nitrenium ion which is generated from sodium azide and trifluoromethanesulfonic acid according to the scheme shown below. As follows from this scheme, the molar ratio $\text{CF}_3\text{SO}_3\text{H--NaN}_3$ should be equal to 2. The amination with $\text{CF}_3\text{SO}_3\text{H--NaN}_3$ taken at the above ratio was successful only in the case of very active substrate, mesitylene, and the corresponding product, 2,4,6-trimethylaniline was obtained in 61% yield. The yield increased to 72% when the molar ratio $\text{CF}_3\text{SO}_3\text{H--NaN}_3$ was raised to 3:1, while further raising the reactant ratio almost did not affect the yield

(75% at a ratio of 4:1). Therefore, we used 3 equiv of trifluoromethanesulfonic acid in the amination of other methylbenzenes.

Methyl-substituted benzene was added to trifluoromethanesulfonic acid, sodium azide was then added to a molar ratio of 1:3:1, and the mixture was subjected to ultrasonic irradiation over a period of 8–11 h and was additionally kept for 4 days at room temperature. The mixture was then treated with a small amount of water, excess 30% aqueous sodium hydroxide was added, the mixture was extracted with diethyl ether, the extract was dried over MgSO_4 , and the solvent was distilled off. The yields of the resulting methyl-substituted anilines were as follows: from toluene, 66% (*o/m/p* ratio 55:9:36); from *o*-xylene, 70% (ratio of 2,3- and 3,4-dimethylanilines 44:56); from *m*-xylene, 70% (ratio of 2,4-, 2,6-, and 3,5-dimethylanilines 71:24:5), from *p*-xylene, 50%; from durene, 21%; from pentamethylbenzene, 24%. The product composition was determined by ^1H NMR spectroscopy (Bruker AC-200 and AV-300) and GC–MS (Hewlett–Packard G 1800A). A Branson 1510 instrument was used for ultrasonic irradiation.

Thus we have demonstrated that electrophilic amination can be successfully performed using stoichiometric amounts of the reactants ($\text{CF}_3\text{SO}_3\text{H}$, NaN_3 , and arene as substrate).



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REFERENCES

1. Borodkin, G.I., Elanov, I.R., Popov, S.A., Pokrovskii, L.M., and Shubin, V.G., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 672.
2. Borodkin, G.I., Popov, S.A., Pokrovskii, L.M., and Shubin, V.G., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 747.
3. Borodkin, G.I., Bessonov, A.A., Andreev, R.V., and Shubin, V.G., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 755.
4. Borodkin, G.I., Elanov, I.R., and Shubin, V.G., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1541.
5. Takeuchi, H., Adachi, T., Nishiguchi, H., Itou, K., and Koyama, K., *J. Chem. Soc., Perkin Trans. 1*, 1993, p. 867.
6. Loupy, A., *Modern Solvents in Organic Synthesis (Topics in Current Chemistry*, vol. 206), Knochel, P., Ed., Berlin: Springer, 1999, p. 153.