Modified Prato reaction for synthesis of 2,5-substituted NH-fulleropyrrolidines

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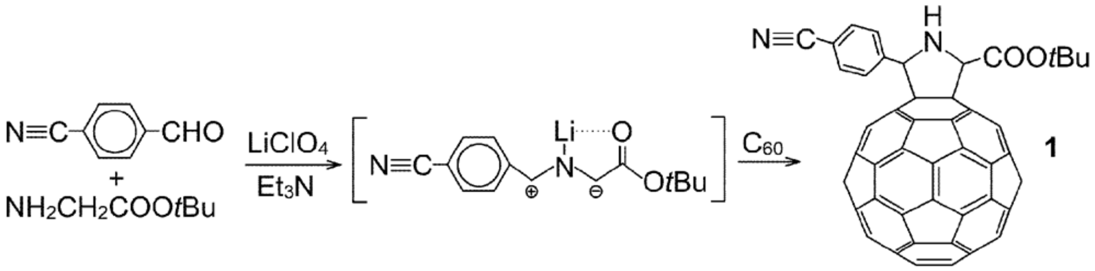
Abroad range of methods of fullerene cage functionalization is aimed at formation of new promising fullerene-based materials that may possess unique biological and technological properties. Among the several successful functionalization methodologies reported in the past years, the Prato reaction is arguably most widely used.

The use of N-unsubstituted amino acids in the Prato reaction for generation of 1,3-dipoles leads to formation of N-unsubstituted fulleropyrrolidines [1].

Here we report a new method of generation of 1,3-dipoles for synthesis of NH-fulleropyrrolidines. Imine derived from condensation of primary amines with aldehydes in presence of soluble in organic solvents lithium salts and organic base forms N-metalated Schiff base [2]. The 1,3-dipole thus obtained is reacted with C_{60} according to 1,3-dipolar cycloaddition.

Thus, for example, interaction of *p*-cyanobenzaldehyde and glycine *tert*-butyl ester in presence of lithium perchlorate and triethylamine leads to formation of N-metalated Schiff base that reacts with fullerene to give 2,5-substituted NH-fulleropyrrolidine **1** according to MALDI mass spectra and ^{1}H NMR analysis.



Advantages of the method reported include high yields (60-70%) and, additionally, possibility of further derivativization of N-unsubstituted fulleropyrrolidines at nitrogen to provide new useful materials.

[1] X. Tan, D.I. Schuster and S.R. Wilson, *Tetrahedron Lett.* **39**, 4187 (1998).

[2] O. Tsuge, S. Kanemasa, M. Yoshioka, *J. Org. Chem.* **53**, 1384 (1988).