Catalytic synthesis of heteroatom-containing homo- and methanofullerenes

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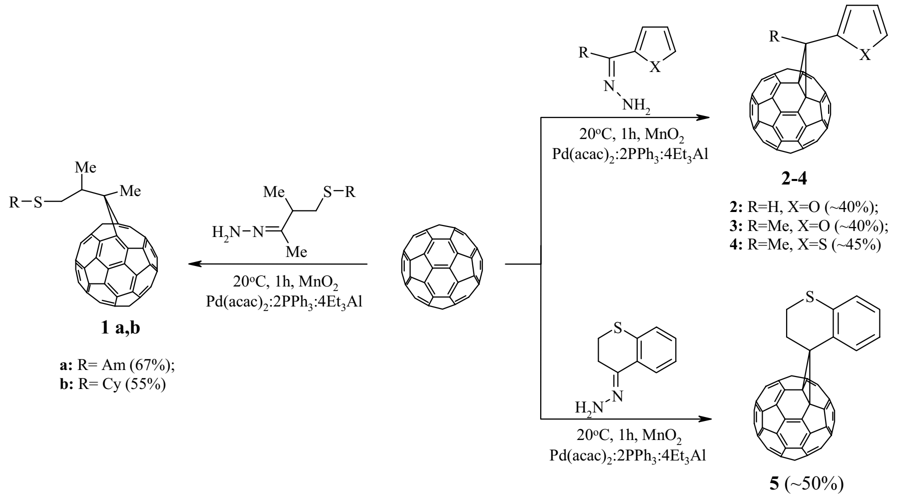
In the report, the efficient methods for selective cycloaddition of heteroatom- containing diazoalkanes to carbon clusters assisted by three-component catalytic system Pd(acac)$_2$-PPh$_3$-Et$_3$Al are presented. The developed methods allow the synthesis of individual homo- and metanofullerenes with high yields and selectivity.

Cycloaddition of S-containing diazoalkanes, generated *in situ* by oxidation of hydrazones of keto sulfides with MnO$_2$, to [60]fullerene (20 ^{o}C, 1 h) assisted by the catalyst Pd(acac)$_2$-2PPh$_3$-4Et$_3$Al leads to 5,6-open cycloadducts **1a** and **1b** in 70% yield with high selectivity. Analysis of ^{1}H and ^{13}C NMR spectral data showed that more bulky substituents at the bridge carbon atom in homofullerene **1** are located above the five-membered fragment of the C$_{60}$ molecule.

In order to expand the application area of the developed catalytic method for cycloaddition of diazoalkanes to [60]fullerene, in this reaction heterocyclic diazo compounds have been involved. The study has revealed that the interaction between hydrazones of furfural, methyl furyl or thienyl methyl ketones and C$_{60}$ under optimized conditions (20 ^{o}C, 1 h, 20 mol % Pd(acac)$_2$-2PPh$_3$-4Et$_3$Al) was found to produce methanofullerenes **2, 3** and **4**. Similar results were obtained in the case of hydrazone tiochroman-4-one. Due to its oxidative stability, hydrazone of 2-acetyl-N-methyl pyrrole remains inert in this reaction and does not produce the desired diazo compound.



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