Functionalization of fluorine-containing fullerene derivatives

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A recently synthesized novel class of the difluoromethylene homofullerenes and a wide range of perfluoroalkylated fullerenes appreciably extend a family of fluorine-containing fullerene derivatives. Due to their high electron-deficient properties these compounds are considered as promising building blocks for organic electronic devices, what may require their additional derivatization. Only a few examples of functionalization of some individual isomers of trifluoromethylated fullerene C_{70} by the Bingel-Hirsch [1] and the Diels-Alder [2] reactions are known. Here we report a new synthetic approach for regioselective derivatization of the novel fluorine-containing fullerene derivatives based on nucleophylic substitution of alkyl halides to their anions.

The reported synthetic approach was applied to the representative compounds from each classes – homofullerene $C_{60}(CF_2)$ and C_s-$C_{70}(CF_3)_8$. The anions of these compounds were chemically generated by the deprotonation of the respective dihydrogenated derivatives [3].

The hydrogenated derivatives, $C_{60}(CF_2)H_2$ and $C_{70}(CF_3)_8H_2$, were synthesized and characterized by UV/Vis-, ^{1}H and ^{19}F NMR spectroscopy. Quantum chemical calculations at the DFT level predict regioselective functionalization of the $C_{60}(CF_2)H^-$ and $C_{70}(CF_3)_8H^-$ due to the localization of negative charge on certain carbon atoms. The deprotonation of the $C_{60}(CF_2)H_2$ and $C_{70}(CF_3)_8H_2$ solutions with consequent treatment by the alkyl halids leads to the formation of the respective alkyl derivatives of the $C_{60}(CF_2)$ and C_s-$C_{70}(CF_3)_8$.

Noteworthy, the reported approach can be applied to the dihydrogenated compounds sequentially to obtain respective disubstituted derivatives.

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[2] Takano Y., Herranz M.A., Kareev I.E., Strauss S.H., Boltalina O.V., Akasaka T., Martin N., *J. Org. Chem*., **74**, 6902 (2009).

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