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Syntheses of Urethano-, Amido- and Sulfonamido-[60]fullerenes by Nucleophilic Substitutions with 1,2-(2,3-Dihydro-1*H*-azirino)-[60]fullerene

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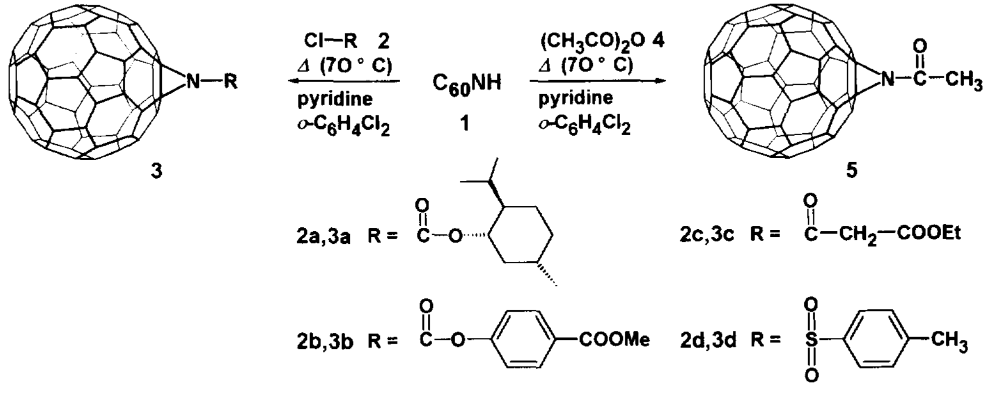
Abstract: $C_{60}NH$ **1** and the acyl and tosyl chlorides **2** or acetic anhydride **4** in 1,2-dichlorobenzene solution and pyridine give the stable fulleroaziridine derivatives **3a-d** and **5** by nucleophilic substitution.

Among the methods of exohedral functionalization of [60]fullerene the syntheses of fulleroaziridines play an important role.[1-5] In general fulleroaziridines are formed by addition of nitrenes to C_{60}[1,2] or by photochemically induced rearrangement of azafulleroids.[3] We have recently reported the synthesis of fulleroaziridines by addition of photochemically generated acylnitrenes[2] and arylnitrenes.[3] In addition we described the synthesis of the parent aziridino-fullerene $C_{60}NH$ (**1**) by elimination of CO_2 and isobutene from 1,2-(*N-tert*-butyloxycarbonyl-4,5-dihydro-1*H*-azirino)-[60]fullerene.[4,5] We are now reporting the syntheses of the urethanes **3a** and **3b**, of the amides **3c** and **5** and of the sulfonamide **3d** by nucleophilic substitution with $C_{60}NH$ (**1**).



The first nucleophilic substitution of a secondary amino-[60]fullerene derivative was the synthesis of *N*-acylated fulleropyrrolidines, which was reported by Maggini, Prato et al.[6] Analogously we also used pyridine as basic reagent. In a typical experiment we slowly added a solution of an excess of the chlorides **2** or acetic anhydride **4** in 10 ml of 1,2-dichlorobenzene to 50 mg (0.068 mmol) of $C_{60}NH$ (**1**)[4] dissolved in 15 ml of a 2:1 mixture of 1,2-dichlorobenzene and pyridine at 70 °C. The substituted fullerenes **3a-d** and **5** were isolated by filtering the reaction mixtures over a silica column (with toluene), followed by evaporation of the solvents in vacuum. Finally the products were purified by a second column filtration over silica with toluene and toluene/*n*-hexane mixtures, respectively (see Table 1).[7] Due to their polar substituents compounds **3** exhibit a much higher solubility than C_{60} in all organic solvents. The ^{13}C NMR (75 MHz) spectra of the fullerene derivatives **3b-d** and **5** show the typical number of fullerene peaks of C_{2v} symmetrical aziridino-

[60]fullerenes[1-5]: 16 lines (13 have a relative intensity of 4, and 3 have a relative intensity of 2 carbons) in the sp^2 region and one signal in the area between 84 and 80 ppm. This indicates a fast rotation around the amide bond as compared to the NMR time scale. Surprisingly the chiral compound **3a** exhibits a different number of fullerene lines in its ^{13}C NMR spectrum.[7] Beside the single resonance of the two sp^3 fullerene carbons at 80.84 ppm we found 22 fullerene resonances (17 have a relative intensity of 2, 3 have a relative intensity of 4, and 2 have a relative intensity of 6 carbons).[7] A ^{13}C NMR experiment at 333 K gave no evidence for the assumption that the unusual number of fullerene resonances is an effect of a similar rate of rotation around the amide bond compared to the NMR time scale.[6] The comparison of the ^{13}C NMR spectra of the compounds **3a** and 1,2-(*N-tert*-butyloxycarbonyl-4,5-dihydro-1*H*-azirino)-[60]fullerene[4] shows that the chemical shifts of the sp^2 fullerene resonances of both resemble one another, but in the case of the (+)-(1S)-menthyl derivative **3a** some of the resonances are splitted. Therefore we assume that the unusual number and splitting of fullerene lines of the chiral compound **3a** are based on diastereotopic fullerene carbons. The UV-VIS spectra of **3** and **4** confirm that they retain the electronic properties of C_{60}.

Table 1

compound	**3a**	**3b**	**3c**	**3d**	**5**
ratio **1**:**2** (**1**:**4**)	1:12.5	1:13	1:25	1:50	(1:57)
reaction time	1h	1h	1h	7h	26h
isolated yield	95%	78%	25%	82%	22%

Compared to the amido-[60]fullerenes **3c** and **5** the sulfonamido-[60]fullerene **3d** and the urethano derivatives **3a** and **3b** are formed in higher yields, which confirms the report of Banks et al. about the quantitative substitution of $C_{60}NH$ **1** with 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose-6-chloroformate by applying similar conditions.[5] In summary, this investigation clearly shows that exohedral functionalizations of fullerenes can be performed even to the second sphere using **1** as a synthetic block of a first sphere-type.

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5. Independently the synthesis of **1** was also reported by: M. R. Banks, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Millar, A. T. Taylor, *J. Chem. Soc., Chem. Commun.* **1995**, 885-886.
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7. The new compounds **3a-d** and **5** show correct mass-spectrometric and spectroscopic data. ^{13}C NMR data of: **3a** (75 MHz, (D_2)-1,1,2,2-tetrachloroethane): δ = 155.93 (C=O), 145.01, 145.00, 144.91, 144.90, 144.64, 144.58, 144.31, 144.29, 144.18, 143.78, 143.56, 143.55, 143.53, 143.51, 142.94, 142.91, 142.54, 141.97, 141.88, 140.94, 140.80, 139.74 (22 sp^2-C fullerene resonances) 80.84 (sp^3-C fullerene resonance), 79.40, 46.86, 40.72, 34.00, 31.45, 25.98, 23.13, 21.97, 20.71, 16.03 ppm. **3d** (75 MHz, (CS_2/CD_2Cl_2 (5:2)): δ = 145.80, 145.64, 145.47, 145.38, 145.32, 144.86, 144.49, 144.33, 144.24, 143.70, 143.50, 143.45, 143.14, 142.53, 142.21, 141.67, 141.27, 136.36, 130.44, 128.87, 80.30, 22.21 ppm.

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