Dihydrothiopyran-fused [60]Fullerene from Hetero-Diels–Alder Reaction with Thioacrylamide and Acyl Chloride

Masatomi Ohno, Satoshi Kojima and Shoji Eguchi*

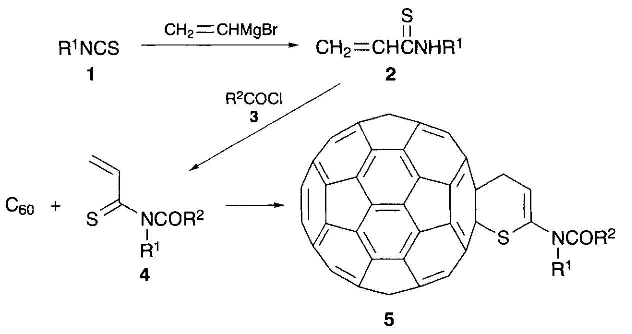
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464-01, Japan

[60]Fullerene undergoes a smooth irreversible hetero-Diels–Alder reaction with an α,β-unsaturated thiocarbonyl compound, prepared *in situ* from thioacrylamide and acyl chloride, to give dihydrothiopyran-fused [60]fullerene cycloadducts.

The cycloaddition methodology is an attractive approach to the formation of 1 : 1 addition products of [60]fullerenes, and a variety of [*m* + *n*]cycloaddition reactions with [60]fullerene as the 2π component have been developed recently.[1] Amongst these the Diels–Alder reaction constitutes a reliable method for the construction of carbocycle-fused [60]fullerene derivatives with, in some cases, an interesting functionality.[2] Heterocycle-fused [60]fullerene derivatives are obtained on the basis of 1,3-dipolar cycloaddition reactions, which provide a method for new carbon–heteroatom bond formation on its surface.[3] The hetero-Diels–Alder reaction is an alternative route,[4] if an appropriate electronic demand in heterodienes is accommodated with [60]fullerene (namely, heterodienes acting as the HOMO). In this respect, α,β-unsaturated thiocarbonyl compounds are potentially useful.[5] They can undergo cycloaddition with reactions electron-deficient dienophiles; and, more conveniently, they tend to suppress retro-Diels–Alder reactions because of the unstable C=S double bond of the diene component. For simplicity of generation and variability of substituents, *N*-acylthioacrylamide **4** was selected, and prepared *in situ* by the reaction of thioacrylamide with acyl chloride (R^2COCl).[6] The thioacrylamide, in turn, is obtained from isothiocyanate (R^1NCS) and vinylmagnesium bromide;[7] thus a variety of substituents R^1 and R^2 can be introduced on the [60]fullerene–heterocycloadduct by combination of these reagents.

The reaction with $R^1 = R^2 = Me$ is a typical example (Scheme 1). Treatment of methylisothiocyanate **1a** with 1 equiv. of vinylmagnesium bromide afforded *N*-methylthioacrylamide **2a** after silica gel chromatography.[7] According to the reported procedure,[6] the freshly prepared thioamide **2a** (5 equiv.) in dry toluene was acylated with acetyl chloride **3a** (10 equiv.) and pyridine (10 equiv.) in the presence of [60]fullerene. Then the reaction mixture was heated at 65 °C for 30 min under an argon atmosphere, during which the solution changed from purple to dark brown. After conventional work-up, flash chromatography on silica gel eluted with toluene–diethyl ether (5 : 1; $R_f = 0.31$) gave dihydrothiopyran-fused [60]fullerene **5aa** in 57% yield (based on consumed [60]fullerene). The structure of the cycloadduct was elucidated by spectral inspections. Firstly FAB-MS confirmed the presence of a 1 : 1 cycloadduct by the molecular ion peak at *m/z* 863, with the base peak at *m/z* 720. The IR spectrum indicated absorptions at 1668 (amide group) and 527 cm^{-1} (characteristic of the [60]fullerene skeleton) and the UV–VIS spectrum contained signals at 215, 255, 316, 436 (characteristic of the 1 : 1 cycloadduct of [60]fullerene)[8] and 615 nm. The required ^1H NMR signals (500 MHz) appeared at δ 2.39 (COMe), 3.45 (NMe), 4.36 (ring CH_2) and 7.08 (C=CH). The last two signals, assigned to the heterocyclic ring protons, were observed as a broad singlet, suggesting free ring-flipping at room temperature. In the ^{13}C NMR spectrum (125 MHz) 24 lines[†] were observed at δ 132–148, owing to the sp^2 carbons of [60]fullerene, including two heterocyclic sp^2 carbons, and 2 lines at δ 69.64 and 72.16 due to the [60]fullerene 6,6-junction sp^3 carbons were also seen, together with several lines at δ 22.28, 35.42, 45.16 and 170.27 (C=O) assignable to the carbons of the dihydrothiopyran ring and its substituents. As 30 lines are expected for the [60]fullerene sp^2 carbons from C_s symmetry, 8 lines seemed to overlap incidentally. Under the same conditions, other derivatives **5ab**, **5ba** and **5bb** were obtained in comparable yields using differing combinations of Me and Ph groups, and were similarly characterized. The results are summarized in Table 1.

This reaction demonstrates that the hetero-Diels–Alder reaction of α,β-unsaturated thiocarbonyl compound is applicable to [60]fullerene, giving an irreversible cycloadduct, and a C–S bond can be formed on the [60]fullerene surface. This is the first example of sulfur-bonded [60]fullerene derivatives with the structure confirmed clearly.[9] In particular, various substituents can be introduced on the heterocycle by employing two kinds of reagents (isothiocyanate and acyl chloride).



Scheme 1

Table 1 Hetero-Diels–Alder reaction of [60]fullerene with thioacrylamide and acyl chloride

R^1	R^2	R^1NCS	R^2COCl	[60]Fullerene cycloadduct (Yield [%])[a]	FAB-MS[b] (*m/z*)
Me	Me	**1a**	**3a**	**5aa** (57%)	863
Me	Ph	**1a**	**3b**	**5ab** (69%)	925
Ph	Me	**1b**	**3a**	**5ba** (43%)	925
Ph	Ph	**1b**	**3b**	**5bb** (43%)	987

[a] Yield based on consumed [60]fullerene. [b] A base peak at *m/z* 720 was always present.

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Footnote

[†] ^{13}C NMR data at the lower region δ (132–148): 132.25, 132.75, 140.39, 141.75, 142.04, 142.31, 142.34 (2C), 142.79, 142.92, 142.94, 143.26, 143.35 (2C), 144.82, 144.86 (2C), 145.69, 145.80 (2C), 145.84 (2C), 145.87 (2C), 146.52 (2C), 146.55, 146.85 (2C), 146.89, 147.92, 148.11.

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