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# Reaction of [60]Fullerene with 5-Imino-1,2,4-thiadiazolidine-3-ones: Formation of New $C_{60}$-fused Heterocycles

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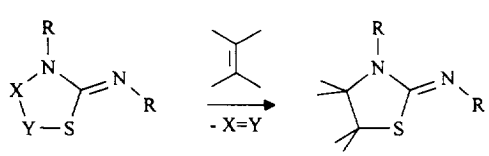
***Abstract.*** Upon refluxing in toluene, [60]fullerene reacts with 5-imino-1,2,4-thiadiazolidine-3-ones **1** to form the 1,2-(3-aryl-2-arylimino-tetrahydrothiazolo)-[60]fullerenes **3**. Copyright © 1996 Elsevier Science Ltd

Chemical modifications of fullerenes by selective bond formation have been intensively explored recently because of the interesting physical and biological properties of derivatives.[1-6] The electron deficient nature of $C_{60}$ opens the pathway to a number of useful reactions. It is well-known that $C_{60}$ is dienophilic which enables the molecule to undergo cycloadditions reactions. Moreover, $C_{60}$ behaves as an 1,3-dipolarophile. Thus, [60]fullerene undergoes Diels-Alder reactions, [3+2], [2+2] and [2+1] cycloadditions with a variety of reagents.[7,8]

We are interested in five-membered cycloadducts containing nitrogen. The background of our studies is to obtain compounds which tolerate a large variety of functional groups. Recently we reported the 1,3-dipolar cycloaddion of pyrazolidinium ylides to [60]fullerene.[9] In this case, the obtained bicyclic γ-lactam structures were not stable enough for carrying out side-chain chemistry. In this paper we report the synthesis of new fullerene-fused 2-imino-1,3-thiazolidines.

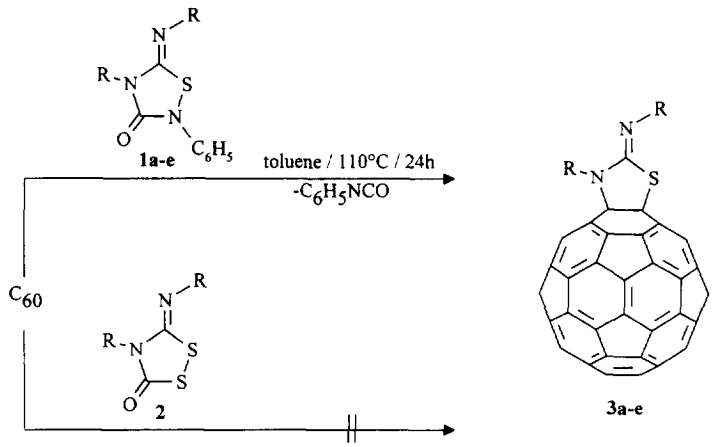
G. L'abbé and coworkers described the reaction of 5-imino-1,2,4-thiadiazolidine-3-ones and related systems as masked 1,3-dipoles. Thus, under elimination of X=Y, isothiocyanates, bis(ethoxycarbonyl)ketene or activated nitriles undergo cycloaddions to give the corresponding imino-thiazolidine derivatives (Scheme 1).[10] We investigated the reaction of $C_{60}$ with the heterocyclic masked 1,3-dipoles **1** and **2** to get new fullerene-fused heterocycles.




Scheme 1. 5-Imino-1,2,4-thiadiazolidine-3-ones as masked dipoles

[60]Fullerene reacts smoothly with compounds **1** upon heating in toluene to give 1,2-(3-aryl-2-arylimino-tetrahydrothiazolo)-[60]fullerenes **3**. Under the same reaction conditions, 5-imino-1,2,4-dithiazolidine-3-one **2** did not react with [60]fullerene (Scheme 2).

The 5-imino-1,2,4-thiadiazolidine-3-ones **1a-e** were prepared by treatment of 5-imino-1,2,4-dithiazolidine-3-ones with isocyanates.[11,12] For the cycloaddition, a solution of 100 mg of $C_{60}$ (138.76 μmol) and 277.52 μmol of the appropriate thiadiazolidinone **1** was kept at reflux in 75 ml toluene under inert conditions (argon) for 24h. The color of the solution turned purple to red brown. Chromatography on silica gel with toluene as eluent yielded unchanged $C_{60}$ (first fraction) and the new fullerene-fused 2-imino-1,3-thiazolidines **3a-e** (second fraction) in 31-71% yield (based on converted $C_{60}$).




| | 3a | 3b | 3c | 3d | 3e |
|---|---|---|---|---|---|
| R | $C_6H_5$ | $C_6H_4$-4-$CH_3$ | $C_6H_4$-4-Br | $C_6H_4$-4-Cl | $C_6H_4$-4-$OCH_3$ |
| yield (%) | 58 | 71 | 46 | 31 | 58 |

Scheme 2. Preparation of cycloadducts **3a-e**

The structure of the fullerene derivatives was identified by standard spectroscopic methods and high resolution LSIMS (for preliminary $FAB^+$ studies cf. ref.[13]). $^1H$ NMR spectra exhibit multiplets for the aromatic protons between 6.7 ppm and 7.8 ppm. The two methyl groups of **3b** give only one singulet at 2.37 ppm ($CDCl_3$/TMS), the two methoxy groups of **3e** two isolated singulets at 3.74 ppm and 3.78 ppm ($CS_2$/TMS). The $^{13}C$ NMR spectra ($CS_2$ or $CD_2Cl_2$, 125.70 MHz; APT investigations) indicate the presence of 30 $sp^2$ fullerene signals for **3a**, **3b** and **3e** (Fig. 1). The halogen derivatives **3c** and **3d** show only 27 lines in the fullerene $sp^2$ region (partly unresolved). All new derivatives give two $sp^3$ signals at 84.9 ppm (fullerene $sp^3$-C-N) and 67.5 ppm (fullerene $sp^3$-C-S) for the reacted fullerene carbons. The intensity of the aliphatic fullerene carbons was enhanced by the addition of relaxation reagent ($Cr(acac)_3$). Fig.1 shows characteristic parts of the spectra **3a** and **3e**. The results of the $^1H$ and $^{13}C$ NMR spectroscopy are only compatible with the $C_S$ symmetrical structure. This is the criterion for a closed 6-6-ring fused 1,2-dihydro-fullerene structure of the derivatives **3a-e**. Table 1 represents the signals of the two different aromatic substituents (Aryl-$sp^2$-N and Aryl-$sp^3$-N). Calculations with increment systems and the comparison of the relatively stable $sp^2$-fullerene signals allowed the exact determination for all chemical shifts of the aromatic carbons.[14] Only the ipso-carbon atom from the derivative **3e** (Aryl-$sp^2$-N) was not detectable. Useful solvents for NMR studies are carbon disulfide or dichloromethane. All spectroscopic methods prove the absence of higher substituted fullerene derivatives than one to one adducts.

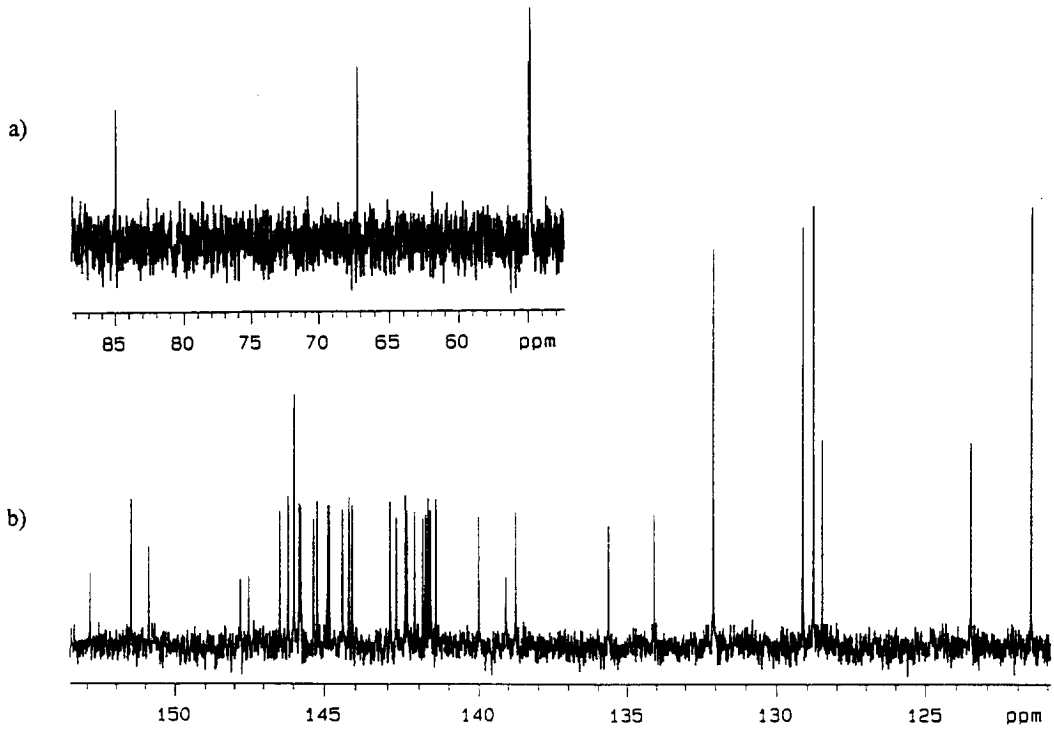



Fig. 1: $^{13}C$ NMR ($CS_2$/TMS/$D_2O$ lock capillary tube) a) aliphatic region of **3e**; b) aromatic region of **3a**.

Tab.1 $^{13}C$ NMR data of **3a-e**; in $CS_2$/TMS/$D_2O$ lock capillary tube.

| | | | | | Aryl-$sp^3$-N in ppm | | | | Aryl-$sp^2$-N in ppm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $sp^3$-C-N | $sp^3$-C-S | C=N | ipso-C | o-C | m-C | p-C | ipso-C | o-C | m-C | p-C |
| **3a** | 84.9 | 67.5 | 152.9 | 139.1 | 128.8 | 132.1 | 128.5 | 150.9 | 121.6 | 129.1 | 123.5 |
| | 86.3 [a] | 68.3 | 155.6 | 140.7 | 129.6 | 132.7 | 129.5 | 152.4 | 122.3 | 130.1 | 124.3 |
| **3b** [b] | 84.9 | 67.4 | 152.6 | 136.6 | 129.9 | 131.9 | 138.3 | 148.6 | 121.5 | 129.4 | 132.4 |
| **3c** | 84.7 | 67.6 | 153.5 | 137.8 | 132.5 | 133.5 | 123.7 | 149.6 | 123.3 | 131.3 | 117.2 |
| **3d** | 84.8 | 67.6 | 153.5 | 137.3 | 129.5 | 133.2 | 135.2 | 149.1 | 122.8 | 128.9 | 129.2 |
| **3e** [c] | 84.9 | 67.2 | 152.8 | 131.6 | 133.0 | 114.3 | 159.2 | - [d] | 122.3 | 114.0 | 155.8 |

a) in $CD_2Cl_2$/TMS; b) $\delta_{Me}$ = 21.5 ppm and 21.1 ppm; c) $\delta_{OMe}$ = 54.9 ppm and 54.8 ppm; d) not resolved

The UV-VIS spectra of **3a-e** in n-hexane exhibit the typical absorptions of dihydrofullerenes. The weak bands at 428-435 nm and 689-692 nm indicate also the cycloaddition at a site of a two six-membered ring junction.[15] In the IR spectra characteristic bands of the fullerene skeleton in the region at 510, 1180 and 1410 $cm^{-1}$ and the very strong band at 1605 $cm^{-1}$ for the C=N-double bond are in agreement with the postulated structure.

## EXPERIMENTAL

### General remarks and materials

5-Imino-1,2,4-thiadiazolidine-3-ones **1a-e** were prepared according to literature.[9,10] [60]Fullerene was used in *gold grade* quality (Hoechst). Toluene were used in *for spectroscopy* quality (Merck, UVASOL). Chromatography was performed on silica gel 60 (Merck, 0.040-0.063 mm). NMR spectra were obtained on a Varian Unity 500 spectrometer at 500 MHz for $^1H$ NMR and 125.70 MHz for $^{13}C$ NMR. Chemical shifts are given in ppm with tetramethylsilane as internal standard. IR spectra were recorded on a Specord 75 (Carl Zeiss, Jena) and are given in $cm^{-1}$. The UV spectra were mesuared on a UV-2102 PC scanning spectrophotometer (Shimadzu) and are given in nm. High-resolution mass spectra were obtained using high resolution LSIMS (Autospec, Fison) with o-nitrophenyl *n*-octyl ether as matrix.

### General Procedure

A solution of 100 mg $C_{60}$ (138.76 µmol) and 277.52 µmol of the appropriate 5-imino-1,2,4-thiadiazolidine-3-one **1** in 75 ml toluene was refluxed under inert conditions (argon) for 24 h. To the cooled solution, 15g of silica gel were added and the solvent evaporated under reduced pressure. The resulting solid was purified by flash chromatography (silica gel 60) with toluene as eluent. The first fraction contains unchanged $C_{60}$, the second fraction the appropriate 2-imino-1,3-thiazolidine derivative **3**.

*1,2-(3-Phenyl-2-phenylimino-tetrahydrothiazolo)-[60]fullerene* (**3a**).

Yield: 46 mg unconverted $C_{60}$; 41 mg **3a** (58%). Exact mass (LSIMS) calc. for $C_{73}H_{10}N_2S^{+\bullet}$: $[M]^{+\bullet}$ 946.0564, found 946.0537; $[M+H]^+$ 947.0642, found 947.0496. $^1H$-NMR (500 MHz; $CD_2Cl_2$): δ = 7.18-7.84 (m, 5H). $^{13}C$-NMR (125.70 MHz; $CS_2$; $Cr(acac)_3$): δ = 152.92, 151.50, 150.90, 147.82, 147.53, 146.46, 146.19, 145.99, 145.82, 145.77, 145.35, 145.24, 144.91, 144.85, 144.43, 144.22, 144.12, 142.93, 142.74, 142.45, 142.40, 142.15, 141.88, 141.78, 141.71, 141.63, 141.47, 141.45, 140.02, 139.10, 138.76, 135.66, 134.10, 132.10, 129.10, 128.82, 128.51, 123.56, 121.58, 84.86, 67.47. IR (KBr): 2900, 1605, 1580, 1495, 1480, 1410, 1320, 1180, 1095, 755, 690, 510. UV/VIS $\lambda_{max}$ in *n*-hexane: 208, 255, 317.5, 428, 680, 692.

*1,2-[3-(4-Methylphenyl)-2-(4-methylphenylimino)-tetrahydrothiazolo]-[60]fullerene* (**3b**).

Yield: 72 mg unconverted $C_{60}$; 27 mg **3b** (71%). Exact mass calc. for $C_{75}H_{14}N_2S$: $[M]^{+\bullet}$ 974.0878, found 974.0861; $[M+H]^+$ 975.0956, found 975.0983. $^1H$-NMR (500 MHz; $CDCl_3$): δ = 7.68 (d, 1H), 7.32 (d, 1H), 7.16 (dd, 2H), 2.37 (s, 6H). $^{13}C$-NMR (125.70 MHz; $CS_2$; $Cr(acac)_3$): δ = 152.64, 151.64, 148.56, 147.80, 147.52, 146.68, 146.17, 145.97, 145.80, 145.75, 145.36, 145.21, 144.89, 144.84, 144.43, 144.36, 144.13, 142.97, 142.77, 142.72, 142.43, 142.38, 142.17, 141.87, 141.78, 141.69, 141.65, 141.47, 139.99, 138.76, 138.34, 136.57, 135.61, 134.10, 132.42, 131.87, 129.85, 129.44, 121.50, 84.90, 67.41, 21.46, 21.11. IR (KBr): 2900, 1610, 1595, 1495, 1410, 1315, 1180, 1095, 810, 510. UV/VIS $\lambda_{max}$ in *n*-hexane: 210, 254, 318.5, 430, 682, 692.

*1,2-[3-(4-Bromophenyl)-2-(4-bromophenylimino)-tetrahydrothiazolo]-[60]fullerene* (**3c**).

Yield: 55 mg unconverted $C_{60}$; 32 mg **3c** (46%). Exact mass (LSIMS) calc. for $C_{73}H_8Br_2N_2S$: $[M]^{+\bullet}$ 1101.8775, found 1101.8731; $[M+H]^+$ 1102.8853, found 1102.8872. $^1$H-NMR (500 MHz; $CS_2$): δ = 7.57 (dd, 2H), 7.36 (d, 1H), 6.94 (d, 1H). $^{13}$C-NMR (125.70 MHz; $CS_2$; $Cr(acac)_3$): δ = 153.46, 150.94, 149.59, 147.83, 147.56, 146.23, 146.02, 145.86, 145.72, 145.29, 145.25, 144.94, 144.86, 144.41, 144.08, 143.91, 142.75, 142.487, 142.44, 142.06, 141.87, 141.77, 141.70, 141.51, 141.49, 140.05, 138.95, 137.79, 135.73, 134.04, 133.48, 132.47, 131.34, 123.68, 123.25, 117.22, 84.75, 67.60. IR (KBr): 2900, 1605, 1570, 1485, 1410, 1310, 1185, 1095, 1070, 1000, 820, 750, 580, 510. UV/VIS $\lambda_{max}$ in *n*-hexane: 252, 327, 404, 420, 591, 690.

*1,2-[3-(4-Chlorophenyl)-2-(4-chlorophenylimino)-tetrahydrothiazolo]-[60]fullerene* (**3d**).

Yield: 34 mg unconverted $C_{60}$; 29 mg **3d** (31%). Exact mass (LSIMS) calc. for $C_{73}H_8Cl_2N_2S$: $[M]^{+\bullet}$ 1013.9785, found 1013.8921; $[M+H]^+$ 1014.9863, found 1014.8624. $^1$H-NMR (500 MHz; $CS_2$): δ = 7.59 (d, 1H), 7.40 (d, 1H), 7.18 (d, 1H), 6.96 (d, 1H). $^{13}$C-NMR (125.70 MHz; $CS_2$; $Cr(acac)_3$): δ = 153.51, 150.95, 149.11, 147.79, 147.52, 146.19, 145.98, 145.82, 145.73, 145.25, 145.22, 144.91, 144.83, 144.38, 144.05, 143.89, 142.72, 142.45, 142.40, 142.03, 141.84, 141.73, 141.67, 141.47, 141.49, 140.02, 138.90, 137.26, 135.69, 135.22, 133.99, 133.21, 129.47, 129.22, 128.87, 122.81, 84.79, 67.58. IR (KBr): 1605, 1570, 1485, 1410, 1315, 1180, 1090, 1065, 1000, 815, 510. UV/VIS $\lambda_{max}$ in *n*-hexane: 207, 255, 318, 420, 460, 689.

*1,2-[3-(4-Methoxyphenyl)-2-(4-methoxyphenylimino)-tetrahydrothiazolo]-[60]fullerene* (**3e**).

Yield: 40 mg unconverted $C_{60}$; 49 mg **3e** (58%). Exact mass (LSIMS) calc. for $C_{75}H_{14}N_2O_2S$: $[M]^{+\bullet}$ 1006.0776, found 1006.0933; $[M+H]^+$ 1007.0854, found 1007.0888. $^1$H-NMR (500 MHz; $CS_2$): δ = 7.53 (d, 1H), 6.89 (dd, 2H), 6.74 (d, 1H), 3.78 (s, 3H), 3.74 (s, 3H). $^{13}$C-NMR (125.70 MHz; $CS_2$; $Cr(acac)_3$): δ = 159.17, 155.79, 152.79, 151.67, 147.76, 147.48, 146.73, 146.13, 145.93, 145.92, 145.76, 145.71, 145.30, 145.16, 144.84, 144.79, 144.39, 144.37, 144.32, 144.10, 142.93, 142.67, 142.38, 142.34, 142.13, 141.83, 141.74, 141.64, 141.61, 141.45, 139.93, 138.75, 135.55, 134.05, 132.98, 131.63, 122.33, 114.22, 113.97, 84.92, 67.17, 54.86, 54.75. $^{13}$C-NMR (125.70 MHz; $CS_2$; $Cr(acac)_3$): δ = 2900, 1605, 1565, 1500, 1410, 1385, 1280, 1230, 1180, 1095, 1005, 905, 810, 680, 590, 510, 450. UV/VIS $\lambda_{max}$ in *n*-hexane: 205, 254, 332, 373, 389, 435, 550, 692.

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