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Addition of Azomethine Ylides to C_{60}: Synthesis, Characterization, and Functionalization of Fullerene Pyrrolidines

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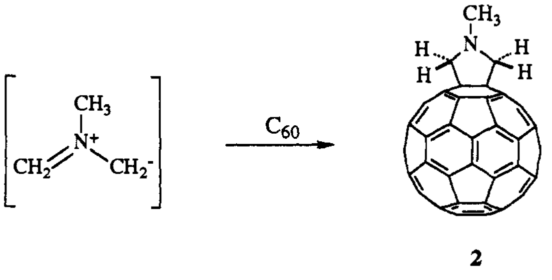
The fascinating physical and chemical properties of fullerene, C_{60},[1] are retained in many of its addition derivatives.[2] Moreover, the solution chemistry of this novel form of carbon becomes richer when new functional groups are introduced.[3] These concepts have stimulated a significant amount of effort aimed at obtaining single-addition, well characterized, fully organic C_{60}-containing compounds.[4] In this context, the strong dipolarophilic character of C_{60} has been disclosed,[5] as well as the high tendency of this fullerene to behave as a reactive 2π component in cycloadditions.[4] In line with these reactivity studies, we report herein a new and very general fullerene functionalization, based on the 1,3-dipolar cycloaddition of azomethine ylides to C_{60}.

Azomethine ylides, planar species of general formula (R^1R^2)-$C{=}N^+(R^3){-}C^-(R^4R^5)$, represent one of the most reactive and versatile classes of 1,3-dipoles.[6] They can be generated from a wide variety of easily accessible starting materials and react readily with a range of dipolarophiles. The products of cycloaddition, substituted pyrrolidines, are well suited for further functionalization.

A very easy way of generating azomethine ylides is the "decarboxylation route".[6b] Thus, a mixture of *N*-methylglycine (sarcosine **1**, 2 molar equiv) and paraformaldehyde (5 molar equiv) was heated at reflux in toluene in the presence of C_{60} (1 molar equiv). The reaction proceeded very smoothly in 2 h, affording the *N*-methylpyrrolidine derivative **2** (eq 1) in 41% yield after chromatography (82% based on C_{60} conversion).

$$CH_3\text{-}NH\text{-}CH_2\text{-}CO_2H + CH_2O \xrightarrow[-\,CO_2]{\Delta}$$

1



(1)

2

The high symmetry of compound **2** is indicated by its NMR spectra.[7] In the ^1H spectrum ($CS_2/CDCl_3$), only two singlets are observed at δ 2.98 (CH_3) and 4.38 (CH_2). The ^{13}C spectrum shows 16 signals (13 signals integrate four carbons each and three signals integrate two carbons) between δ 155 and 136 as well as three peaks at δ 41.5 (CH_3), 70.0 (CH_2), and 71.1 (two carbons). This latter signal is attributed to the sp^3 fullerene carbons. These findings are only compatible with the C_{2v} symmetrical structure **2** and account for a dipole attack on a 6,6 ring fusion of C_{60}. The UV–vis spectrum of **2** shows that the pyrrolidine derivative retains the main electronic features of C_{60} (Figure 1), although a new absorption is now present at 306 nm. This particular band (whose nature has yet to be defined) has not been reported previously for C_{60} derivatives and might deserve deeper examination. FABMS exhibited a relevant peak at *m/e* 778 (MH^+, 58%, base peak at *m/e* 720, C_{60}^+).[8]

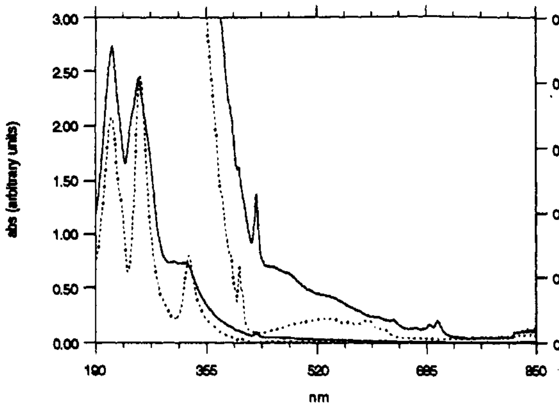
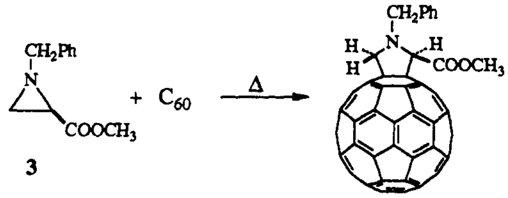


Figure 1. UV–vis spectra of **2** (solid line) and C_{60} (dotted line) in cyclohexane.

Another approach to azomethine ylides, the thermal ring-opening of aziridines,[6] gave the same profitable results. Heating **3** and C_{60} in toluene at reflux led to the isolation in 40% yield of the new pyrrolidine derivative **4** (73% based on C_{60} conversion, eq 2).



3

4

(2)

The present new fullerene functionalization offers high potential in the materials chemistry field. Of the several uses that can be envisioned, two representative examples are reported below.

When 3-triphenylmethyl-5-oxazolidinone (**5**)[9] was heated at reflux for 16 h in toluene with C_{60} in equimolar amount, compound **6** was isolated in 39% yield (72% based on C_{60} conversion) after chromatography (Scheme I, Trt = triphenylmethyl). Exposure of **6** to the action of trifluoromethanesulfonic acid gave a precipitate which was centrifuged and then suspended in methylene chloride. Addition of pyridine and dansyl chloride (DnsCl) to this suspension brought about the isolation in 76% yield of the dansyl pyrrolidine derivative **8**. The intermediacy of the amine

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[1] (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

[2] See, for example: Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186.

[3] For a remarkable elaboration of C_{60} derivatives, see: Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656.

[4] Taylor, R. Walton, D. R. M. *Nature* **1993**, *363*, 685.

[5] The 1,3-dipolar cycloaddition reactions of C_{60} with diazo compounds and azides has been extensively studied by Wudl and co-workers: (a) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157. (b) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148.

[6] (a) Lown, J. W. In *1,3-Dipolar Cycloaddition Chemistry*, Padwa, A., Ed.; Wiley: New York, 1984. (b) Tsuge, O.; Kanemasa, S. *Adv. Heterocycl. Chem.* **1989**, *45*, 231.

[7] As expected, nitrogen inversion is fast as compared to the NMR time scale.

[8] Please see supplementary material.

[9] Tsuge, O.; Kanemasa, S.; Ohe, M.; Takenaka, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4079.

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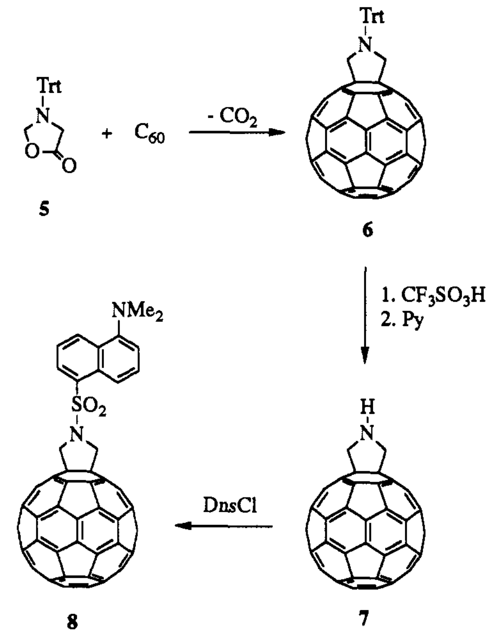
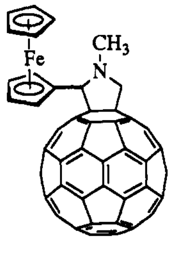
Scheme I



7 is clearly involved here.[10] Although it is known that amines add to C_{60},[11] 7 was reasonably stable at ambient temperature in dilute solutions and decomposed only upon concentration.[12] Here, the possibility of further reacting 7 with a series of electrophiles can be seen as an extremely versatile approach to many functionalized fullerenes.

The covalent attachment of a photoactive moiety to C_{60} can be of special interest for the investigation of the optical properties of the fullerenes. In the present case, while it is known that dansyl pyrrolidine itself is a powerful fluorescing agent,[13] no luminescence was observed in the 400–600-nm interval upon irradiation of compound **8** at 330 nm.[14] The details of this study will be reported in due course.

Materials containing two different, covalently linked redox centers are very appealing for applications in molecular electronics.[15] The combination of two electroactive species like C_{60} and ferrocene in a single unit can be achieved with our methodology for the realization of a unique redox assembly. By heating a mixture of ferrocene aldehyde, sarcosine, and C_{60} in toluene at reflux, compound **9** was isolated in 57% yield after chromatography.[16]



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The cyclic voltammetry of this interesting substrate in acetonitrile/toluene showed both reduction and oxidation patterns of the C_{60} and ferrocene moieties.[17] Further studies and applications of this novel redox system are currently underway.

Acknowledgment. We are deeply indebted to Prof. Fred Wudl, University of California–Santa Barbara, who introduced us to the "art" of functionalizing C_{60}. We thank Prof. G. Gennari and Mr. S. Darin (Padova, Italy) for help in luminescence measurements. We also thank Prof. S. Daniele (Venezia, Italy) and Dr. G. Sandonà (Padova, Italy) for preliminary CV experiments.

Supplementary Material Available: Detailed experimental procedures and full characterization of compounds **2**, **4**, **6**, **8**, and **9** (27 pages). Ordering information is given on any current masthead page.

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[10] The presence of **7** has been confirmed by FABMS (MH^+ =764 *m/e*) and also by reaction with acetic anhydride to give the corresponding *N*-acetyl derivative.

[11] Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1309.

[12] The product of decomposition of **7**, probably an oligomer, was not investigated.

[13] Drory, A.; Thompson, J. E.; Mayak, S.; Borochov, A. *J. Plant Physiol.* **1992**, *140*, 544.

[14] For an example of luminescence quenching involving electron transfer to C_{60}, see: Sacrifitci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.

[15] Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

[16] Cocrystallization of C_{60} and ferrocene and X-ray structure determination of the resulting C_{60}(ferrocene)$_2$ complex has been reported: Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1764.

[17] Cyclic voltammograms were recorded at –40 °C in toluene/acetonitrile 75/25 under nitrogen atmosphere by using a conventional three-electrode configuration: glassy carbon as working electrode and platinum wires as reference and auxiliary electrodes. A 0.1 M *n*-Bu_4NClO_4 solution was used as supporting electrolyte, and potentials were referenced to Fc/Fc^+ as internal standard. Reversible reduction waves were observed at potentials $E_{1/2} = -1.13$, –1.52, –2.08, and –2.49 V. In the anodic part, one reversible oxidation peak was observed almost overlapping the added ferrocene reference.