JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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J. Am. Chem. Soc., **2007**, 129 (47), 14580-14581 • DOI: 10.1021/ja077927k

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Reversible Microwave-Assisted Cycloaddition of Aziridines to Carbon Nanotubes

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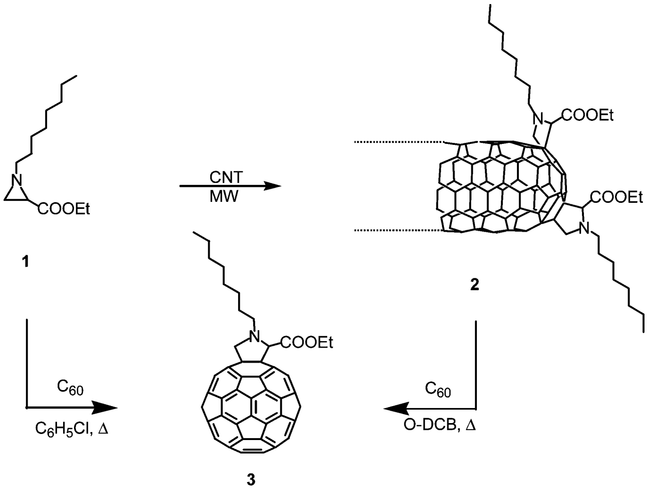
The fascinating properties of carbon nanotubes (CNTs) make them suitable for applications in many fields, such as electronics, materials engineering, nanomedicine, etc.[1] In some cases, their covalent functionalization is required, mainly to allow the unique properties of CNTs to be combined with those of other types of materials. A few methods have been developed to this purpose and have been widely used.[2] Most of these reactions use conventional chemical techniques, such as refluxing and/or sonication in organic solvents or mineral acids, often making use of high temperatures or pressures,[3,4] long reaction times,[5] or highly reactive species.[6] Consequently, alternative functionalization approaches are highly desirable to enable new protocols, simple to execute, and easy to scale-up.

Microwave-assisted organic synthesis enhances the rate of reactions and improves product yields, as well as energy efficiency.[7] The response of carbon nanotubes to electromagnetic radiation in the absence of solvent has been the subject of many recent investigations.[8] A sample of pristine HiPco SWNTs displays strong microwave absorption with subsequent dramatic light emission and intense heat release; this fact has been used for nanotube purification.[9] In the presence of solvents or in dense and viscous environments, there is not such a strong response, while the behavior of nanotubes is similar to that of other organic compounds under microwave irradiation. Recently, microwave radiation has been used to assist CNT functionalization in the presence of strong oxidants[10] to synthesize a soluble derivative of short SWNTs,[11] to enable cycloadditions to prefunctionalized CNTs,[12] or to perform radical additions.[13] However, no attempts have been reported, so far, to use this technology for the functionalization of CNTs employing the strong microwave absorption typical of pristine nanotubes. In this paper, we report the first study of microwave-assisted cycloaddition to pristine CNT in solvent-free conditions.

Aziridines are well-known precursors to azomethine ylides, which represent an important class of 1,3-dipoles in cycloaddition reactions.[14] Since azomethine ylides have been successfully added to fullerenes and carbon nanotubes, aziridines are also expected to react.[2,15] Single-wall carbon nanotubes (SWNTs, HiPco lot # R0496) were suspended in a dichloromethane (DCM) solution of aziridine **1** (Scheme 1). The mixture was sonicated for 5 min, then the solvent was evaporated. The flask containing SWNTs finely suspended in oily **1** was irradiated in solvent-free conditions in a CEM focused microwave, model Discover. Reactions were carried out in a closed quartz tube with control of pressure. After 1 h of irradiation, the functionalized SWNTs (f-SWNTs) **2a** were separated from the solution by filtration over a Millipore membrane (Fluoropore, 0.2 μm), washed with DCM, and characterized using different techniques, such as Raman and UV−vis−NIR spectroscopies, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). To increase the degree of functionalization, the overall sequence was repeated another two times, giving rise to f-SWNTs **2b** and **2c**, respectively. Nanotubes **2c** were slightly soluble in DMF and dichloromethane (0.13 and 0.11 mg/mL, respectively, Figure S12).

Scheme 1



The TGA of compounds **2a**, **2b**, and **2c** presents a loss of weight of about 20, 23, and 27%, respectively, at 600 °C compared to about only 4% of the pristine SWNTs, which corresponds to the presence of one functional group for about 76, 63, and 51 carbon atoms, respectively (Figure 2a). This is consistent with the increase of the D-band observed in the Raman spectra (Figure 1, exciting line = 632.8 nm). While the spectrum of the starting material displays a small disorder mode at 1314 cm^{-1}, its intensity gradually increases with the number of groups added covalently to the surface of the nanotubes. Furthermore, we observe a D-band shift to lower frequencies (1308 cm^{-1} for **2c**). The Raman spectrum shows that the microwave-assisted functionalization preserves all the types of nanotubes. In fact, the radial breathing mode (RBM) spectral region below 400 cm^{-1} (see inset to Figure 1) shows that the spectra of the pristine SWNTs and that of **2c** have the same bands for both semiconducting nanotubes, above 230 cm^{-1}, and metallic nanotubes, below this frequency,[16] although some intensity variation can be observed, in particular, for metallic nanotubes which are probably

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10.1021/ja077927k CCC: $37.00

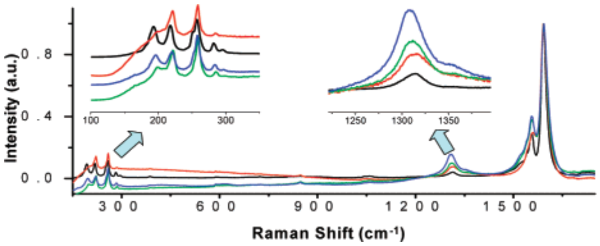

Figure 1. Normalized Raman spectra of pristine SWNTs and f-SWNTs **2a**, **2b**, and **2c**.

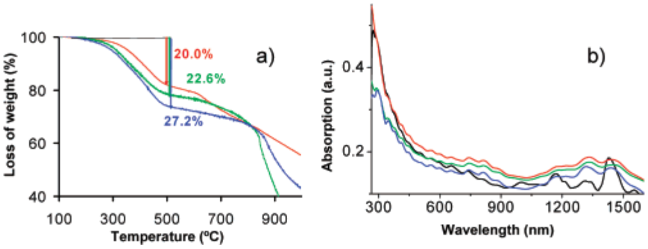

Figure 2. (a) TGA of f-SWNTs **2a**, **2b**, and **2c**. (b) UV−vis−NIR in DMF of pristine SWNTs and f-SWNTs **2a**, **2b**, and **2c**. Color codes: pristine SWNTs (black); f-SWNTs **2a** (red), **2b** (green), and **2c** (blue).

more easily functionalized.[17] Figure 2b shows also the characteristic interband transitions between van Hove singularities of pristine HiPco nanotubes and the partial loss of these transitions in the functionalized samples as usually observed when functionalization is performed.[18]

To assess the efficiency of our procedure, SWNTs were functionalized with aziridine **1** in DMF using a similar protocol in classical conditions for azomethine ylides.[15] Under these conditions, the reaction proceeds in 5 days (against 1 h under microwave irradiation). The TGA of these tubes shows a weight loss of 12%, which corresponds to one functional group for about 138 carbon atoms (Figure S3). These results confirm the efficiency of the microwave-mediated protocol described here. In the absence of solvent, the radiation is absorbed directly by the reagents, in this case by CNTs, so that the effect of microwaves is more marked. The use of this protocol is also interesting because environmentally friendly synthesis can be easily designed, the use of large amount of solvents is avoided, and the workup procedures are considerably simplified.

The present procedure can be used to easily scale-up the reaction. To this aim, 250 mg of multi-wall carbon nanotubes (MWNTs, from Nanoamorphous and Nanostructured Carbon, Houston, Texas, lot # RX1804) was allowed to react with aziridine **1**, in 1 h, using the microwave protocol already shown for SWNTs. These f-MWNTs are soluble in solvents such as DMF and CH_2Cl_2 (0.55 mg/mL in CH_2Cl_2 and 0.40 mg/mL in DMF) (Figure S13), and their TGA showed a weight loss of 6% (Figure S5).

Martín and co-workers[19] have reported the retro-cycloaddition of pyrrolidinofullerenes using a variety of different efficient dipolarophiles. In our case, 250 mg of f-MWNTs was heated to 150 °C in *o*-dichlorobenzene (O-DCB) for 48 h with $CuTf_2$ as catalyst, in an excess of C_{60} in order to trap the corresponding ylide that results from the thermal retro-cycloaddition (Scheme 1). At the end of the reaction, the nanotubes were separated from the residue by filtration over a Millipore membrane (Fluoropore, 0.2 μm). The recovered nanotubes exhibited no solubility in any solvent. TGA data confirmed the loss of functional groups, while the TEM images showed a highly pure material. In the filtrate, the presence of fullerene monoadduct **3** was proven by TLC and by HPLC, by comparison with an authentic sample. This latter was prepared by direct cycloaddition reaction of aziridine **1** to C_{60} (Scheme 1). The same procedure was performed using f-SWNTs. Also in this case, the recovered nanotubes showed no solubility, whereas images of clean material were observed by TEM. The reduced D-band in the Raman spectra and the minimal weight loss in TGA also confirmed the retro-cycloaddition (Figures S8−S11).

This result indirectly confirms the pyrrolidine structure on f-CNT after cycloaddition. Its direct assessment is made impossible by the low solubility and the difficulty to obtain a reasonably resolved NMR spectrum.

In conclusion, we have developed a new approach that uses microwaves to rapidly functionalize CNTs by using 1,3-dipolar cycloaddition of aziridines. An indirect proof of the covalent sidewall functionalization of the tubes has also been provided. The application of this microwave approach to different precursors to azomethine ylides is currently being explored in our labs and will be reported soon.

Acknowledgment. The authors are grateful to DGICYT of Spain for financial support through project CTQ2007-60037/BQU, and to Consejería de Educación y Ciencia through projects PAI-05-019 and PBI-06-0020, and the University of Trieste and MUR (PRIN 2006, prot. 2006034372 and Firb RBIN04HC3S). A travel grant from Italy−Spain Integrated Action is gratefully acknowledged. Technical assistance from Mrs. Noelia Rubio is also acknowledged.

Supporting Information Available: Experimental procedures, characterization data for **1** and **3**, TGA and TEM images of f-MWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA077927K