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Sidewall Epoxidation of Single-Walled Carbon Nanotubes: A Theoretical Prediction

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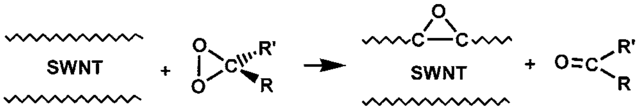
ABSTRACT



By means of a two-layered ONIOM approach, we predict that sidewall epoxidation of single-walled carbon nanotubes (SWNTs) with dioxiranes is viable. The SWNT epoxides thus produced could be precursors for further chemical modification of SWNTs, given the abundant and well-established chemistry of organic epoxides. This opens the door for routine chemical manipulation of SWNTs.

Increasing interest has recently been focused on the chemical functionalization of single-walled carbon nanotubes (SWNTs)[1] due to their potential applications in nanoelectronics technology.[2] Successful approaches toward chemically functionalized SWNTs so far reported can be divided into three categories, namely, covalent functionlization of the sidewalls, defect functionalization, and noncovalent (supramolecular) functionalization.[1] Among these, covalent sidewall functionalization appears to be rather challenging, as the graphene-like sidewalls of SWNTs display high chemical stability. Yet several experiments successfully approaching covalent sidewall derivatization have been reported, including fluorination,[3] addition of alkyl radicals,[4] [2 + 1] cycloaddition,[4,5] 1,3-dipolar cycloaddition,[6] electrochemical and solvent-free arylations,[7] ozonolysis,[8] osmylation,[9] etc. Meanwhile, theoretical predictions also have been made on the viability of sidewall derivatization of SWNTs by ozonization,[10] 1,3-dipolar cycladdition,[10,11] [4 + 2] cycloaddition,[12] osmylation,[13] and [2 + 1] cycloaddition.[14] In this communication, we report a theoretical prediction on the viability of sidewall epoxidation of SWNTs with dioxiranes.

So far, no experiment has been reported regarding the epoxidation of SWNTs. Dioxiranes are highly reactive oxidants; an important application of dioxiranes in synthetic

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(1) For recent reviews on chemical modifications of carbon nanotubes, see: (a) Hirsh, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853. (b) Bahr, J. L.; Tour, J. M. *J. Mater. Chem*. **2002**, *12*, 1952. (c) Sun, Y.-P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res*. **2002**, *35*, 1096.

(2) (a) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603. (b) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996; pp 1–985. (c) Dekker, C. *Phys. Today* **1999**, *52*, 22. (d) Dai, H. *Phys. World* **2000**, *13*, 43. (e) Ouyang, M.; Huang, J.-L; Lieber, C. M. *Acc. Chem. Res*. **2002**, *35*, 1018. (f) Avouris P. *Acc. Chem. Res*. **2002**, *35*, 1026.

(3) (a) Mickelson, E. T.; Huffmann, C. B.; Rinzler, A. G.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *Chem. Phys. Lett.* **1998**, *296*, 188. (b) Khabashesku, V. N.; Billups, W. E.; Margrave, J. L. *Acc. Chem. Res*. **2002**, *35*, 1087 and references therein.

(4) Holzinger M.; Vostrovsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002.

(5) (a) Chen, Y.; Haddon, R. C.; Fang, S.; Rao, A. M.; Lee, W. H.; Dickey, E. C.; Grulke, E. A.; Pendergrass, J. C.; Chavan, A.; Haley, B. E.; Smalley, R. E. *J. Mater. Res.* **1998**, *13*, 2423. (b) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon R. C. *Science* **1998**, *282*, 95.

(6) (a) Georgakilas, D.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc*. **2002**, *124*, 760. (b) Georgakilas, V.; Voulgaris, D.; Vazquez, E.; Prato, M.; Guldi, D. M.; Kukovecz, A.; Kuzmany, H. *J. Am. Chem. Soc*. **2002**, *124*, 14318.

(7) (a) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc*. **2001**, *123*, 6536. (b) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156.

(8) Banerjee, S.; Wong, S. S. *J. Phys. Chem. B.* **2002**, *106*, 12144.

(9) Cui, J. B.; Burghard, M.; Kern, K. *Nano Lett.* **2003**, *3*, 613.

(10) Lu, X.; Zhang, L.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, *106*, 2136.

(11) Lu, X.; Tian, F.; Xu, X.; Wang, N.; Zhang, Q. *J. Am. Chem. Soc.* **2003**, *125*, 10459.

(12) Lu, X.; Tian, F.; Wang, N.; Zhang, Q. *Org. Lett*. **2002**, *4*, 4313.

(13) Lu, X.; Tian, F.; Feng, Y.; Xu, X.; Wang, N.; Zhang, Q. *Nano Lett.* **2002**, *2*, 1325.

(14) Lu, X.; Tian, F.; Zhang, Q. *J. Phys. Chem. B* **2003**, *107*, 8388.

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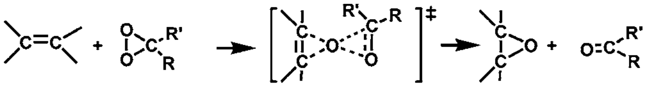
Scheme 1. Epoxidation of Olefins with Dioxiranes



organic chemistry is the epoxidation of olefins (Scheme 1).[15] The high reactivity of dioxiranes in olefin epoxidation has been demonstrated by numerous investigations.[15,16] In general, the epoxidation proceeds readily with electron-rich olefins.[15] However, a successful attempt was also made to employ dioxiranes as oxidants for the epoxidation of the highly electron-deficient and π-conjugated [60] fullerene,[17] another allotrope of carbon. This led us to explore theoretically the viability of sidewall-epoxidation of SWNTs with dioxiranes.

We first considered the epoxidation of an armchair (5,5) SWNT with difluorodioxirane (DFDO), dioxirane (DO), and methyl(trifluoromethyl)dioxirane (MTFDO). A two-layered ONIOM(B3LYP/6-31G*:AM1) approach[18,19] has been used to explore the epoxidation processes on the (5,5) tubewall; the (5,5) SWNT is represented by a $C_{130}H_{20}$ model tube, in which the high-level part is a C_{16} cluster with 10 H atoms as boundary atoms. Details of such a modeling scheme can be found in our previous reports[10−14] (see also Supporting Information). Similar modeling approaches were employed by other groups in the study of carbon nanotube chemistry.[20] All calculations were performed with Gaussian98.[21] The predicted activation energies and reaction heats for the sidewall epoxidations of (5,5) SWNT with these dioxiranes are given in Table 1. The corresponding transition states (**TS1**−**TS3**) as well as the sidewall epoxide (**ep5**) are depicted in Figure 1. For comparison, the predicted activation energies and reaction heats for the epoxidations of ethylene with these dioxiranes are also listed in Table 1.

Table 1. Predicted Activation Energies (E_a) and Reaction Heats (E_r) for the Epoxidation with Difluorodioxirane (DFDO), Dioxirane (DO), and Methyl(trifluoromethyl)Dioxirane (MTFDO) (Given in Units of kcal/mol)

		DFDO	DO	MTFDO
(5,5) SWNT[a]	E_r	−51.8	−41.9	−42.4
	E_a	5.4	20.6	22.4
C_2H_4[b]	E_r	−62.4	−52.5	−53.1
	E_a	−0.1[c]	13.2	11.0

[a] Data obtained by two-layered ONIOM(B3LYP/6-31G*:AM1) calculations. [b] Data obtained at the B3LYP/6-31G* level of theory. [c] Molecular complex precursor 2.3 kcal/mol lower in energy than isolated reactants was found in the B3LYP/6-31G* calculation.

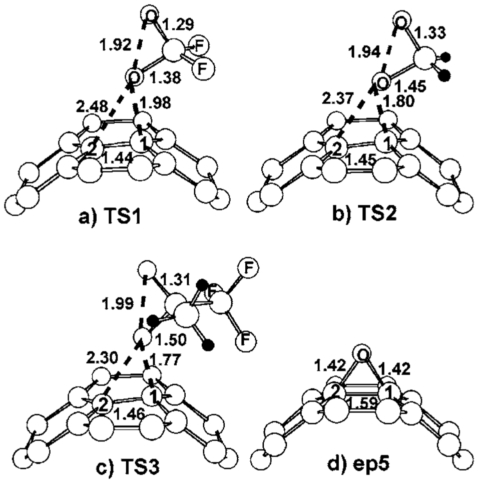


Figure 1. Optimized geometries (local view) of the transition states (**TS1** for DFDO, **TS2** for DO, and **TS3** for MTFDO) and sidewall epoxide (**ep5**) for the sidewall epoxidations of (5,5) SWNT.

The reaction of DFDO with the (5,5) tubewall is predicted to be exothermic by 51.8 kcal/mol with an activation energy of 5.4 kcal/mol (at the transition state **TS1**). The epoxidations with DO and MTFDO are less exothermic and require higher activation energies (20.6 kcal/mol for DO and 22.4 kcal/mol for MTFDO). Thus, DFDO appears to be the most powerful oxidant for sidewall epoxidation, and all concerned epoxidations are viable on the (5,5) tubewall, giving rise to a sidewall epoxide species **ep5**. Due to the high π-conjugation within the tubewall, these heterogeneous sidewall epoxidations are far less efficient than their molecular

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(15) (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (b) Adam, W.; Hadjiarapoglou, L. P.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; p 195.

(16) For recent theoretical investigations on the epoxidation of olefins, see: Bach, R. D.; Dmitrenko, O.; Adam, W.; Schambony, S. *J. Am. Chem. Soc.* **2003**, *125*, 924 and references therein.

(17) (a) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S; Alvarez, M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351. (b) Manoharan, M. *J. Org. Chem.* **2000**, *65*, 1093.

(18) For the ONIOM approach, see: (a) Maseras, F.; Morokuma, K. *J. Comp. Chem.*, **1995**, *16*, 1170. (b) Dapprich, S.; Komáromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *J. Mol. Struct.* (*THEOCHEM*) **1999**, *461/462*, 1.

(19) For the hybrid density functional B3LYP method, see: (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. A* **1988**, *37*, 785. For the AM1 method, see: (c) Dewar M.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4499.

(20) (a) Bauschlicher, C. W. *Chem. Phys. Lett.* **2000**, *322*, 237. (b) Bauschlicher, C. W. *Nano Lett.* **2001**, *1*, 223. Froudakis, G. E. *Nano Lett.* **2001**, *1*, 179. (c) Froudakis, G. E. *Nano Lett.* **2001**, *1*, 531. (d) Froudakis, G. E. *J. Phys.: Condens. Matter* **2002**, *14*, 453. (e) Basiuk, E. V.; Basiuk, V. A.; Banuelos, J.-G.; Saniger-Blesa, J.-M.; Pokrovskiy, V. A.; Gromovoy, T. Y.; Mischanchuk, A. V.; Mischanchuk, B. G. *J. Phys. Chem. B* **2002**, *106*, 1588. (f) Basiuk, V. A.; Basiuk, E. V.; Saniger-Blesa, J.-M. *Nano. Lett.* **2001**, *1*, 657. (g) Basiuk, V. A. *Nano Lett.* **2002**, *2*, 835. (h) Chakrapani, N.; Zhang, Y. M.; Nayak, S. K.; Moore, J. A.; Carroll, D. L.; Choi, Y. Y.; Ajayan, P. M. *J. Phys. Chem. B* **2003**, *107*, 9308.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

analogues, i.e., ethylene epoxidations, as indicated by the higher exothermicities and lower activation energies predicted for the molecular reactions (cf. Table 1). It should be noted that the order of reactivity for the sidewall epoxidations with the three dioxiranes, i.e., DFDO $\gg$ DO $>$ MTFDO, does not fully coincide with the order of reactivity for the ethylene epoxidations, i.e., DFDO $\gg$ MTFDO $>$ DO. This can be tentatively ascribed to the larger repulsion between MTFDO and the tubewall in the transition state **TS3**. Furthermore, as depicted in Figure 1, these heterogeneous processes adopt highly asymmetric transition states, differing largely from their molecular analogues that prefer symmetric transition states.[16]

To see how the reactivity of sidewall epoxidation depends on the diameter of SWNTs, we further considered the epoxidatons of armchair (n,n) SWNTs (n = 6, 8, 10) with DFDO. The activation energies and reaction heats for these reactions predicted by two-layered ONIOM(B3LYP/6-31G*:AM1) calculations (see Supporting Information for details) are listed in Table 2, together with the SWNT diameters and the pyramidalization angles of tubewall C atoms. The predicted exothermicity for the sidewall epoxidation ranges from 51.8 kcal/mol on the (5,5) tube to 38.7 kcal/mol on the (10,10) tube, while the activation barrier ranges from 5.4 kcal/mol on the (5,5) tube to 8.0 kcal/mol on the (10,10) tube. Thus, sidewall epoxidation is viable on all concerned armchair SWNTs and follows a trend that the larger diameter the SWNT has, the lower reactivity (i.e., lower exothermicity and higher reaction barrier) displayed by the nanotube sidewall. Such diameter dependence of sidewall reactivity can be attributed to the curvature-induced pyramidalization of the tubewall C atoms.[22] Note that the pyramidalization angle of tubewall C atoms in these SWNTs decreases with the increasing of tube diameter. Since the diameter range (6.8−13.9 Å) of this series of SWNTs coincides with the diameter range (7−11 Å) of the commercially available HiPco SWNTs,[23] the sidewall epoxidation of HiPco SWNTs with the use of DFDO would be quite plausible in practice.

Table 2. Activation Energies (E_a) and Reaction Heats (E_r) for the Epoxidation of (n,n) SWNTs (n = 5, 6, 8, 10) with Difluorodioxirane; Diameters and Pyramidalization Angles (PAs) of Tubewall C Atoms Are Also Presented

	(5,5) tube	(6,6) tube	(8,8) tube	(10,10) tube
E_r (kcal/mol)	−51.8	−47.2	−41.9	−38.7
E_a (kcal/mol)	5.4	6.3	7.3	8.0
diameter (Å)	6.8	8.4	11.2	13.9
PA[a] (deg)	5.97	4.99	3.74	3.00

[a] Data adapted from ref 22a.

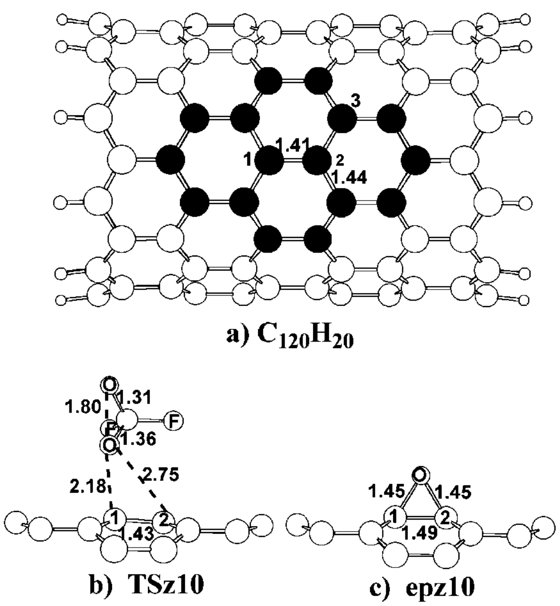

Figure 2. (a) $C_{120}H_{20}$ model tube representing a zigzag (10,0) SWNT, in which the 16 shaded C atoms together with 10 H atoms as boundary atoms are used for the high-level treatment of the two-layered ONIOM(B3LYP/6-31G*:AM1) calculations. (b) Local geometry (side view) of the transition state (**TSz10**) for the reaction of DFDO with the tubewall. (c) Local geometry (side view) of the sidewall epoxide (**epz10**).

Further effort has been made to explore the sidewall epoxidation on a zigzag (10,0) SWNT (diameter ≈ 7.9 Å). With the use of a $C_{120}H_{20}$ model tube (Figure 2a),[20g] preliminary ONIOM(B3LYP/6-31G*:AM1) calculations predict an activation energy of 2.8 kcal/mol and an exothermicity of −34.8 kcal/mol for the reaction of DFDO on the tubewall, indicating that the reaction is feasible, too. The transition state (**TSz10**) for the sidewall epoxidation of the (10,0) tube and the resulting sidewall epoxide (**epz10**) are depicted in Figure 2. Similar to that on the armchair SWNTs, the transition state for the reaction on the zigzag (10,0) tube is also highly asymmetric. It is interesting to note that the reaction on the zigzag (10,0) tube is even less exothermic than that on the armchair (10,10) tube, despite that the latter has a much larger diameter than the former. Such a difference implies that the epoxidation of the sidewalls of carbon nanotubes might be highly helicity-dependent. Note that a chemical or physical property that is highly helicity-dependent is very important for the separation of metallic SWNTs from semiconducting SWNTs.[24] On the other hand, we should mention that our calculations were carried out by

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(22) (a) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 1105. (b) Chen, Z. F.; Thiel, W.; Hirsch, A. *ChemPhysChem* **2003**, *4*, 93.

(23) (a) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C. B.; Rodriguez-Macias, F. J.; Boul, P. J.; Lu, A. H.; Heymann, D.; Colbert, D.; T.; Lee, R. S.; Fischer, J. E.; Rao, A. M.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A: Mater. Sci. Process.* **1998**, *67*, 29. (b) Ichida, M.; Mizuno, S.; Tani, Y.; Saito, Y.; Nakamura, A. *J. Phys. Soc. Jpn.* **1999**, *68*, 3131.

(24) (a) Krupke, R.; Hennrich, F.; Löhneysen, H. v.; Kappes, M. M. *Science* **2003**, *301*, 344. (b) Strano, M. S.; Huffman, C. B.; Moore, V. C.; O'Connell, M. J.; Haroz, E. H.; Hubbard, J.; Miller, M.; Rialon, K.; Kittrell, C.; Ramesh, S.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2003**, *107*, 6979.

using tubes with finite lengths. A subtle difference was predicted in the chemical reactivities of armchair SWNTs with different lengths,[10,11,25] e.g., in our ONIOM calculations of the ozonization of armchair (5,5) SWNT, the use of two model tubes, $C_{90}H_{20}$ and $C_{130}H_{20}$, results in a difference of 7.4 kcal/mol in the predicted reaction heat, along with a much smaller difference (1.5 kcal/mol) in the prediction of activation energy.[10,11] Further elaborate investigation should be done to see in what manner the chemical reactivities of finite-length zigzag SWNTs would change with increases in the tube length.

In summary, by means of two-layered ONIOM calculations, we predict that sidewall epoxidation of SWNTs with dioxiranes is viable. Such heterogeneous epoxidation would become even more feasible in protic solvents (solvent catalysis).[16] It should be noted that apart from dioxiranes, other oxidants such as peroxy acids (RCO_3H) and hypofluorous acid (HOF) are also capable of epoxidizing olefins[16,26] and fullerenes.[27] Whether these oxidants can be used for the epoxidation of SWNTs remains unclear and deserves further theoretical and experimental investigations. Moreover, the sidewall epoxides thus produced can be precursors for further chemical modification of SWNTs, given the abundant and well-established chemistry of organic epoxides.[28] For example, epoxides are reactive to nucleophilic agents such as alcohols (ROH) and amines (RNH_2),[28a] providing a way to anchor a wide variety of functional groups on the sidewalls of SWNTs.[10] Thus, sidewall epoxidation could be a stepping stone to rational chemical manipulation of SWNTs.

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Supporting Information Available: Details of the ONIOM(B3LYP/6-31G*:AM1) modeling scheme, optimized geometries of the transition states for the sidewall epoxidations of (n,n) SWNTs ($n = 6, 8, 10$) and the corresponding sidewall epoxides. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Matsuo, Y.; Tahara, K.; Nakamura, E. *Org. Lett.* **2003**, *5*, 3181.

(26) Rozen, S. *Acc. Chem. Res.* **1996**, *29*, 243.

(27) Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8926.

(28) (a) Cram, J. M.; Cram, D. J. *The Essence of Organic Chemistry*, Addison-Wesley Publishing Co.: Reading, MA, 1979; Chapter 5. (b) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (c) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421.