by a 450-W Hanovia lamp using a uranium glass filter under nitrogen. The reaction was followed by TLC and GC using column a; no starting material was detected after 2 h of irradiation. The solvent was removed at reduced pressure to give the photoadducts in 94% yield. The two isomers were separated by preparative GC, oven temperature 210 °C, to give 46 mg of **12** and 46 mg of **13**. **12**: IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (60 MHz, C_6D_6) δ 0.916 (3 H, d, J = 6 Hz); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1369. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.59; H, 10.24. **13**: IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (60 MHz, C_6D_6) δ 0.87 (3 H, d, J = 6 Hz); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1364. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.78; H, 9.96.

Irradiation of Enone Olefin 3. A solution of **3** (0.185 g, 0.9 mmol) in 150 mL of cyclohexane was irradiated as described for **1** to give a mixture of two photoadducts in a 1:1 ratio according to GC analysis on column a, in 90% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.81 (6 H, d, J = 6 Hz); HRMS calcd for $C_{14}H_{22}O$ 206.1670, found 206.1676.

Irradiation of Enone Olefin 5. A solution of **5** (0.05 g, 0.3 mmol) in 28 mL of cyclohexane was irradiated by an 80-W Philips lamp via a uranium glass filter for 3 h under nitrogen. The solvent was removed under reduced pressure, and the oil was purified by preparative GC to give, in 92% yield, the photoadducts **17** and **18**: IR ($CHCl_3$) 1690 cm^{-1}; HRMS calcd for $C_{11}H_{14}D_2O$ 166.1326, found 166.1324.

Irradiation of Enone Olefin 6. Enone **6** (0.032 g, 1.8 mmol) was irradiated for 3 h as described for **5**. The reaction was followed by GC using column a; the photoadducts were isolated in 95% yield. Two products were identified, **19** and **20**, in a 35:1 ratio, respectively, by GC analysis on column a. **19**: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.07 (3 H, d, J = 6 Hz); HRMS calcd for $C_{12}H_{18}O$ 178.1357, found 178.1347. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.77; H, 10.11.

Irradiation of Enone Olefin 7. Enone **7** (0.045 g, 0.25 mmol) was irradiated for 3 h as described for **5**. The reaction was followed by GC using column a; photoadducts **19** and **20** were formed in a 5.8:1 ratio and were isolated in 95% yield. Spectral data of the mixture: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ_{19} 1.07 (3 H, d, J = 6 Hz), δ_{20} 0.93 (3 H, d, J = 6 Hz). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.80; H, 10.13.

Irradiation of Enone Olefin 8. Enone **8** (0.029 g, 0.14 mmol) was irradiated for 4 h as described for **5**. The reaction was followed by GC using column b; photoadducts **21** and **22** were formed in a 3.8:1 ratio and were isolated in 90% yield. Spectral data of the mixture: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.90 (6 H, d, J = 6 Hz), 0.80 (6 H, d, J = 6 Hz). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.51; H, 10.99.

Irradiation of Enone Olefin 9. Enone **9** (0.021 g, 0.1 mmol) was irradiated for 4 h as described for **5**. Photoadducts **21** and **22** were formed in 1.4:1 ratio, according to GC using column b, and isolated in 90% yield.

Irradiation of Enone Olefin 10. Enone **10** (0.142 g, 0.86 mmol) was irradiated as described for **1**, and a single photoadduct, **23**, was isolated in 95% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 2.43 (1 H, m), 2.34 (1 H, m), 2.31 (1 H, m), 1.93 (2 H, m), 1.8–1.7 (2 H, m), 1.64 (1 H, m), 1.59–1.5 (2 H, m), 1.4–1.3 (5 H, m) 1.14 (1 H, m); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1205.

Irradiation of Enone Olefin 11. Enone **11** (0.023 g, 0.14 mmol) was irradiated as described for **5**. The photoadduct was isolated in 92% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^2H NMR (400 MHz, C_6D_6) δ 2.43 (1 D, s), 1.57 ($^2/_3$ D, s), 1.32 ($^1/_3$ D, s); HRMS calcd for $C_{11}H_{14}D_2O$ 166.1327, found 166.1310.

Supplementary Material Available: ^1H NMR spectra for relevant compounds (18 pages). Ordering information is given on any current masthead page.

Notes

Preparation of Fullerenes with a Simple Benchtop Reactor

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Received April 15, 1991

Though the de novo synthesis of buckminsterfullerene, C_{60}, remains an interesting challenge to the organic chemist,[1] the fullerenes are currently prepared by electric-arc graphite decomposition[2,3] in machines that are the domain of chemical physicists, physicists, materials scientists, and electrical engineers. Basically, an arc between two graphite rods is sparked at 60–150 A in a He (100 Torr) atmosphere in a commercial metal evaporator and the soot resulting from the decomposition is collected, extracted with toluene, and separated by chromatography.[4] A rather complicated machine, for more efficient preparations, in which two $^1/_4$-in. rods are held horizontally and kept in arcing contact manually by a screw mechanism, has recently been described.[5] More recently, mixtures of fullerenes ("soot extract") were made commercially available,[6] albeit at relatively high price.

In this publication, we describe a fullerene benchtop reactor that is easily assembled from commercial preparative chemistry glassware and a minimum of machine shop work (total cost, parts and labor $700). The apparatus is shown schematically below and in full detail in

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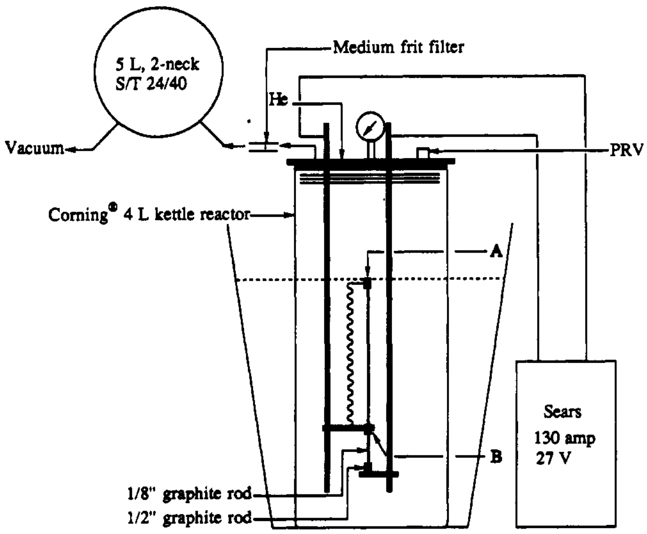
[5] Haufler, R. E.; Chai, Y.; Chibante, L. P. F.; Conceicao, J.; Jin, C.; Wang, L. S.; Maruyama, S.; Smalley, R. E. *Mat. Res. Soc. Symp. Proc.* **1991**, in press.

[6] Materials & Electrochemical Research Corp. (MER Corp.), 7960 So. Kolb Rd., Tucson Az 85706; $250/100 mg, $1200.00/1000 mg. Texas Fullerene Corp.; $100/10 g of crude soot. We thank Prof. R. Smalley for this information.



The key features are that (a) the graphite is gravity-fed[7] and (b) the soot is all neatly contained[8,9] in a familiar reaction vessel. With this apparatus we were able to prepare 0.5 g of soot extract/day (~0.25 g of C_{60}/day), using 3-mm ($^1/_8$-in.) diameter "consumable" rods. The bottom 12-mm ($^1/_2$-in.) diameter graphite rod is essentially not degraded. It takes approximately 10 min to "burn" ~150-mm (6 in.) of graphite when the current is 55 A and ~20 min for the apparatus to cool down. At higher currents (120–150 A), 6 in. of graphite are consumed in only 1 min; however, the yield decreases to 1–2%. Eight runs can be accommodated in 1 day, producing ~6–12 g of soot. Though the yield is only ca. $^1/_2$ that obtained by us with a conventional evaporator, we believe the convenience and simplicity of the apparatus should make it possible for any synthetic chemist to be able to produce useful quantities of C_{60} and C_{70}.

Experimental Section

Reagents. Unless otherwise indicated, all materials were obtained from commercial suppliers and used without purification. Latex gloves and Dust-Mist masks (3M No. 8710) were worn whenever handling the soot or extract.[9] Fisher ultra-spec 2000 gray spectacles were worn while the graphite rods were burning.[10] UV–vis spectra were obtained using a Perkin-Elmer Lambda 5 spectrophotometer. Infrared spectra were obtained as KBr mull pellets using a Perkin-Elmer 1330 spectrophotometer, and NMR spectra were obtained on a GN 500 spectrometer. Power supply was a Sears Craftsman 230/140 AC/DC Infinite Amp Arc Welder. The original cables were modified so they could be bolted onto the electrodes. To avoid any strain on the electrode, the cables were clamped to the top of the reactor. The $^1/_8$-in. high-uniformity graphite rods were obtained from POCO Graphite Inc., 1601 S. State St., Decatur, TX 76234 (catalog no. S55P0H21). The $^1/_2$-in. Specpure graphite rods were obtained from Johnson Matthey Chemicals Limited, 74 Hatton Garden, London, E.C.1. England (catalog no. JMC2103).

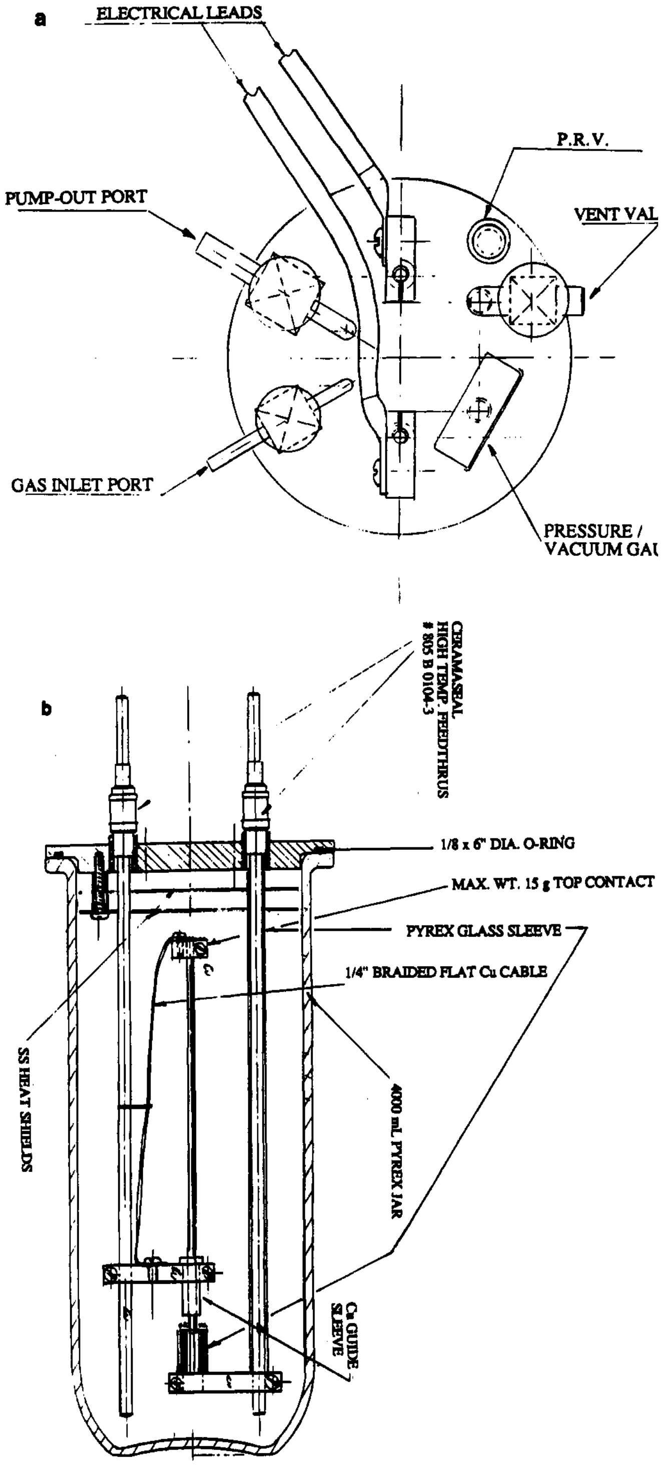


Figure 1. Detailed drawing of the fullerene benchtop reaction. (a) Top view of the aluminum lid, P.R.V. = pressure relief valve. The lid is $6^1/_2$ in. in diameter and $^5/_8$-in. thick aluminum. A 3/4-in. bevel was turned to seat the lid on the reactor, followed by a 6-in. diameter groove for the O-ring (see side view, Figure 1b). (b) Side view of the apparatus where most of the components on the lid were left off for clarity. The $^1/_4$-in. diameter Cu electrodes were silver-soldered to the ceramaseals, which were, in turn, silver-soldered to brass pipe threads. As a precaution, one of the $^1/_4$-in. Cu electrodes and the $^1/_2$-in. graphite rod were lined with a Pyrex sleeve.

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[7] The UCLA modified evaporator used the idea of gravity graphite feed: Whetten, R. L.; Alvarez, M. M.; Anz, S. J.; Schriver, K. E.; Beck, R. D.; Diederich, F. N.; Rubin, Y.; Ettl, R.; Foote, C. S.; Darmanyan, A. P.; Aborgast, J. W. *Mat. Res. Soc. Proc.* **1991**, *206*, in press, private communication, 1990.

[8] C_{60} is a very efficient sensitizer for the conversion of triplet to excited-state singlet oxygen as determined by: Aborgast J. W.; Darmanyan, A. P.; Foote, C. S.; Diederich, F. N.; Whetten, R. L.; Rubin, Y. *J. Phys. Chem.* **1991**, *95*, 11.

[9] The combination of photophysics[8] and electrochemical properties (Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050) of C_{60} should be of some health-related concern, see: Foote, C. S.; Diederich, F.; Whetten, R. L.; Wudl, F. *Chem. Eng. News* **1990**, *68*, 2. Hence the use of masks and gloves in our Experimental Section.

[10] As a reviewer pointed out, one should never look at the arc itself even with protective eye glasses; however, after ~30 s of soot generation, the walls of the vessel are so dark that no light escapes and only an orange-to-white glow can be observed just below the cooling baffles. The same reviewer suggests placing a shield in front of the apparatus, as a precaution. We have never observed any explosive changes in pressure; we even had an accidental O-ring leak *for several runs in a row* without noticeable sudden pressure changes.

Formation of Fullerenes. One end of an 8-in. long, $^{1}/_{8}$-in. diameter, graphite rod was sharpened with a pencil sharpener, then weighed (~2.8 g). The flat end of the $^{1}/_{8}$-in. rod was secured to part A (see diagram above) and placed through the copper guide B (see diagram above), so that the point was resting in an indent carved into the $^{1}/_{2}$-in. graphite rod. The apparatus was connected to an ultrapure He cylinder and to a two-neck 5-L round-bottom flask (ballast). The second neck of the ballast was connected to an oil vacuum pump via a 2.5-cm outside diameter coarse frit to prevent soot from contaminating the oil pump. The apparatus was purged five times by He pump-filling cycles. The setup was then brought to 100 Torr He. The reactor was placed in a cold water bath (5-gal bucket), the power supply was set to 130 A, AC, and turned on. After the arc between graphite rods started, the power was reduced to a setting of "70" (ammeter reading of 55 A). In about 10 min. the $^{1}/_{8}$-in. rod was consumed (~6 in.) to the point that it could no longer make contact with the $^{1}/_{2}$-in. rod, and the power was shut off. The system was brought up to atmospheric pressure with He and allowed to cool for 20 min before moving the reactor to a hood and brushing the soot from the electrodes and the heat shield (baffle) into the kettle and extracted with 700 mL of benzene and the extract filtered using a 150-mL ASTM 10-15 M fritted-glass funnel. Sometimes "slag" forms on the $^{1}/_{2}$-in. bottom graphite rod; it should be removed before the next run, otherwise the $^{1}/_{8}$-in. rod will not burn uniformly or it will be difficult to start an arc. Another $^{1}/_{8}$-in. rod was put in place, and the process was repeated. This was done eight times at which point the kettle was moved into a hood. The solvent was removed in vacuo, giving 410 mg of extract from a total of 5.3 g of "burned" carbon (yield 7.7%). Pure C_{60}, 220 mg (53.7% by weight from extract), and C_{70}, 50 mg (~11% by weight from extract, still containing some C_{60}), were obtained by passing the extract through a column of Brockmann neutral activity grade I, 80-200-mesh Alumina, using 5 and 20% toluene in hexanes[4], respectively. When rods were burnt at 6 in./min with 130-A current, 12.5 g of graphite produced only 380 mg of extract (yield ~3%).

Summary and Conclusions

We described an apparatus for the facile preparation of buckminsterfullerenes. The reactor can be assembled mostly from commercial parts and fits in a standard preparative chemist's fume hood. The soot generated from graphite decomposition is easily and safely recovered. The yield of C_{60} is in the range of 3-4% based on graphite rod consumed.

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933 and CHE89-08323. We are indebted to Rudi Stuber and his colleagues for help with the design and execution of the fullerene benchtop reactor.

Supplementary Material Available: Reproduction of photographs of the reactor (3 pages). Ordering information is given on any current masthead page.

Stereoselective Synthesis of Theonelladins A-D[†]

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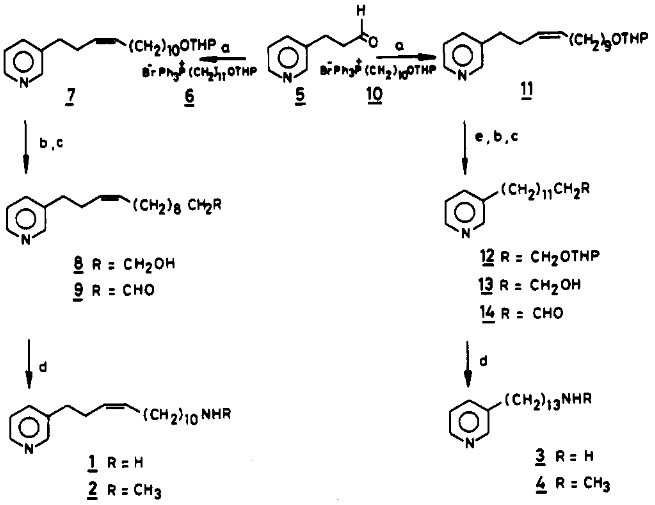
Introduction

In recent years several pyridine-derived alkaloids such as navenones,[1] pulo'upone,[2] halitoxins,[3] and niphatynes,[4] have been isolated from marine organisms. Theonelladins A-D[5] (1-4) belonging to the same group of alkaloids have been isolated from the Okinawan marine sponge *Theonella swinhoei*. The antileukemic Theonelladins A-D also exhibited potent antineoplastic activity against marine lymphomas L1210 and showed powerful Ca^{2+}-releasing activity from sarcoplasmic reticulum. These compounds were found to be 20 times more potent than caffeine, a well-known Ca^{2+} inducer. Here we describe the first total synthesis of these highly active compounds. This process will make it possible to obtain the title compounds in large quantities for biological screening.

Scheme I[a]



[a] Reagents and conditions: (a) *n*-BuLi, THF, 0 → -40 °C; (b) 3 N HCl, MeOH; (c) Swern oxidation; (d) NH_3 or $MeNH_2$, MeOH, $NaBH_4$; (e) Pd-C/H_2, EtOH.

Discussion of Results

The general strategy (Scheme I) utilized in the present synthesis involved a common approach for construction of the required carbon skeleton. Accordingly, the Wittig reaction has been utilized to our advantage, both for the chain elaboration as well as for the stereoselective introduction of the required C-9 double bond. The commercially available 3-γ-pyridinepropanol was chosen as the starting material for simple and straightforward synthesis of 1-4.

Swern oxidation[6] of 3-γ-pyridinepropanol in CH_2Cl_2 gave the aldehyde 5 in 78% yield. Construction of the required carbon skeleton was achieved by Wittig olefination,[7] where the aldehyde 5 in THF was reacted with phosphonium salt[8] 6 in the presence of *n*-butyllithium at -40 °C to afford compound 7, thereby stereoselectively introducing the cis double bond. The configuration of the double bond was assigned by spectral studies (^1H and ^{13}C NMR). The coupling constant of the olefinic protons was found to be 10.6 Hz, corresponding to the literature value.[9] The ^{13}C

[†] IICT Communication No. 2728.

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[5] Kobayashi, J.; Murayama, T.; Ohizumi, Y.; Sasaki, T.; Ohta, T.; Nozoe, S. *Tetrahedron Lett* **1989**, *30*, 4833.

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