naphthyl)mercuric acetate (4) with 2,3-dihydrofuran (5) was carried out in a variety of solvents (Table II). The results establish that the reaction proceeds in both protic and aprotic solvents although in protic solvents (methanol and acetic acid) the yields are quite low. A side product formed in every instance is 1-methoxynaphthalene (13). In acetonitrile solvent, in which the desired arylated dihydrofuran 12 is produced in 90% yield, 13 occurs to the extent of only 7%; in dichloromethane and tetrahydrofuran much larger quantities of 13 are produced at the expense of 12.[18]

Experimental Section

General Comments. NMR spectra were obtained with deuteriochloroform solution by using a JEOL FX90Q spectrometer. Mass spectra were recorded by using either a CEC (Du Pont) 21-110 or a Du Pont 21-491 mass spectrometer. High-resolution measurements were carried out by Dr. T. Wachs, Cornell University, using an AEI MS-902 spectrometer. Column chromatography was performed by using the method of Still.[19] High-pressure liquid chromatography was performed by using a Waters Associates instrument and octadecylsilane columns with methanol–water mixtures as eluants.

(4-Methoxyphenyl)mercuric Acetate (2). Mercuric acetate (31.8 g, 0.1 mol) was dissolved in 200 mL of methanol by heating. To this solution were added 32.4 g (0.3 mol) of anisole and 0.5 mL of perchloric acid with stirring. After 2 days, the precipitate which formed was removed by filtration. Overnight refrigeration of the filtrate resulted in an additional crop. The combined crude product was recrystallized from methanol to yield 13.4 g (37%) of (4-methoxyphenyl)mercuric acetate[12] (2).

(4-Methoxynaphthyl)mercuric Acetate (4). A mixture of 1-methoxynaphthalene (15.8 g, 0.1 mol), mercuric acetate (31.8 g, 0.1 mol), and 0.5 mL of perchloric acid in 200 mL of methanol was stirred at room temperature for 2 days. The precipitated product was collected by filtration and recrystallized from toluene to yield 36 g (87%) of (4-methoxynaphthyl)mercuric acetate (4): mp 222 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (OAc), 4.00 (OCH_3), 6.80 (d, C-3 H, enhanced upon irradiation of OCH_3 resonance), 7.33 (d, C-2 H). Anal. Calcd for $C_{13}H_{12}HgO_3$: C, 37.5; H, 2.90. Found: C, 37.6; H, 2.84.

(2-Methoxy-1-naphthyl)mercuric Acetate (3). A mixture of 2-methoxynaphthalene (5 g, 0.03 mole, mercuric acetate (9.8 g, 0.03 mol), and 0.5 mL of perchloric acid in 75 mL of methanol was heated until solution was achieved and then stirred for 7 days. The mixture was then cooled in an ice bath, and precipitated crude product was collected by filtration and recrystallized from toluene to yield 9.5 g (74%) of (2-methoxy-1-naphthyl)mercuric acetate: mp 106 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.21 (OAc), 3.75 (OCH_3), 7.20 (d, C-3 H, enhanced upon irradiation of OCH_3 resonance). Anal. Calcd for $C_{13}H_{12}HgO_3$: C, 37.5; H, 2.90. Found: C, 37.2; H, 2.88.

Procedure for Palladium-Mediated Coupling of Arylmercuric Acetates with Enol Ethers. To a suspension of 0.12 mmol of an arylmercuric acetate and 0.12 mmol of palladium acetate in 5 mL of acetonitrile was added 0.24 mmol of an enol ether. The resulting mixture was stirred at room temperature for 24 hours and then filtered through Celite. The solvent was evaporated from the filtrate under reduced pressure, and the residue was separated by preparative thin-layer chromatography on silica gel with chloroform. Product yields are in Table I and characterizing spectrometric data are recorded in Table III.

In Table II are yields obtained in coupling of 4 and 5 under conditions identical except that various reaction solvents were used.

Acknowledgment. This research was supported by a grant from the National Institute of General Medical Science (GM 30310).

(18) Changes in palladium and mercuric salt counterions can also dramatically affect reaction course. See ref 6 and: Arai, I.; Hanna, R.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 7684.

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Registry No. 1, 65904-27-0; 2, 5780-90-5; 3, 84132-72-9; 4, 84132-73-0; 5, 1191-99-7; 6, 110-87-2; 7, 1487-15-6; 8, 111-34-2; 9, 84143-13-5; 10, 84132-74-1; 11, 84132-75-2; 12, 84132-76-3; 13, 2216-69-5; 14, 84132-77-4; 15, 84132-78-5; 16, 84132-79-6; 17, 84132-80-9; 18, 84132-81-0; 19, 24764-66-7; mercuric acetate, 1600-27-7; anisole, 100-66-3; 1-methoxynaphthalene, 2216-69-5; 2-methoxynaphthalene, 93-04-9; palladium acetate, 19807-27-3; acetonitrile, 75-05-8; dichloromethane, 75-09-2; tetrahydrofuran, 109-99-9; methanol, 67-56-1; acetic acid, 64-19-7.

Preparation of Oxygen-18-Labeled *m*-Chloroperoxybenzoic Acid

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During the course of our investigation[2] of oxygen transfer from oxaziridines we required a means of preparing these oxaziridines with an ^{18}O label. This was seen as an opportunity for the development of methodology suitable for the preparation of a wide variety of ^{18}O-labeled compounds.[3,4]

We report here a convenient synthesis of ^{18}O-labeled *m*-chloroperoxybenzoic acid which utilizes $^{18}O_2$ as the commercially available isotope source. Oxygen gas, 50% enriched in ^{18}O, was used in 29% efficiency to produce the peroxy acid 39% enriched in ^{18}O at the active oxygen position.[5]

The apparatus illustrated in Figure 1 was constructed for the oxidation of sodium metal by $^{18}O_2$ at elevated temperatures to yield $Na_2{}^{18}O_2$. Several runs with unlabeled O_2 consistently resulted in peroxide containing 70–80% active oxygen. The sodium peroxide was allowed to react with *m*-chlorobenzoyl chloride[5] to yield the desired peroxy acid containing 99% active oxygen. This reagent was found to be efficient in label transfer in the oxidation of diverse substrates (Table I).

Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Bruker WM-270 (270 MHz) NMR spectrometer. Chemical shifts are reported downfield from tetramethylsilane (Me_4Si, internal reference) on the δ scale. Infrared spectra were recorded on a Perkin-Elmer 283B grating infrared spectrometer. GLC/MS analyses were performed on a Varian MAT-44 mass spectrometer interfaced to a Varian Series 1400 gas–liquid chromatograph using He as carrier gas (8 ft × $^1/_8$ in., 4.1% Carbowax column on Chromosorb G). Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Labeled O_2 was obtained from Cambridge Isotope Laboratories, Inc.

(1) Current address: Genentech, Inc., 460 Point San Bruno Blvd., South San Francisco, CA, 94080.

(2) (a) Rastetter, W. H.; Wagner, W. R.; Findeis, M. A. *J. Org. Chem.* **1982**, *47*, 419. (b) Rastetter, W. H., Frost, J. W., *Tetrahedron Lett.* **1979**, 3353.

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(4) ^{18}O-Labeled hydrogen peroxide has been prepared. See: Ball, R. E.; Edwards, J. O.; Jones, P. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2458.

(5) The 39% value was determined from the intensities of the M^+ peaks at *m/e* 174, 176, and 178 adjusted for the presence of two Cl isotopes (see mass spectroscopic data in the Experimental Section).

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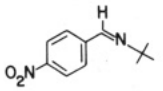
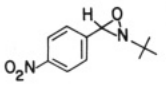
Table I. ^{18}O-Labeled *m*-Chloroperoxybenzoic Acid Oxidations[a]

substrate	reaction time, h	temp, °C	product	% yield	(M + 2)$^+$/M$^+$ ratio
	2	0		70[b]	0.38
	3	25		84[c]	0.36[d]
	3	25		92[c]	0.39[d]

[a] 1.2 equiv of *m*-chloroperoxybenzoic acid used in CH_2Cl_2. [b] Isolated yield. [c] GLC yield. [d] GLC/MS analysis.

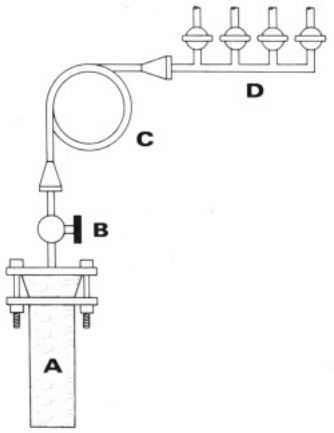


Figure 1. Apparatus for the preparation of $Na_2{}^{18}O_2$: (A) aluminum reaction vessel with Teflon gasket, (B) isolation valve, (C) copper tubing coil, (D) Swagelok manifold with stopcocks to vacuum, manometer, N_2, and $^{18}O_2$. The vessel outer dimensions are 110 mm × 35 mm (40 mm at top), and the wall thickness is 4 mm. Vessel temperature is determined by wrapping a thermometer in heating tape to the outer surface.

Preparation of ^{18}O-Labeled Na_2O_2. Cleaned sodium (1.50 g, 65.2 mmol) was placed into an aluminum reaction vessel (Figure 1; note that *Pyrex will not withstand the extreme reaction conditions*!) which was then evacuated and heated to 300–325 °C, using heating tape. $^{18}O_2$ (1 L, 44.6 mmol, 50% enriched) was opened to the reaction vessel. The vessel was agitated to break the initial oxide coating after which further oxidation proceeded rapidly. When oxygen was no longer being consumed, the vessel was cooled and opened under a nitrogen atmosphere. The powdery contents were finely ground and returned to the vessel. After evacuation and reheating (300–325 °C) of the vessel, additional $^{18}O_2$ (1 L, 44.6 mmol, 50% enriched) was opened to the vessel and allowed to react overnight. The resulting yellow $Na_2{}^{18}O_2$ (2.24 g, 34% based on $^{18}O_2$; active oxygen content 71%, determined by iodometric titration) was used immediately.

Preparation of ^{18}O-Labeled *m*-Chloroperoxybenzoic Acid.[6] THF (5 mL) was placed into a 100-mL, three-necked, round-bottomed flask fitted with an addition funnel and thermometer. $Na_2{}^{18}O_2$ (2.17 g, 20.7 mmol) was added, and the mixture was cooled to −20 °C in a CCl_4–dry ice bath. Into the funnel was placed *m*-chlorobenzoyl chloride (3.36 g, 19.2 mmol) and THF (5 mL). This solution (1.5 mL) was slowly added to the $Na_2{}^{18}O_2$ mixture. $MgSO_4 \cdot 7H_2O$ (50 mg, 0.2 mmol) in H_2O (0.5 mL) was cooled to 0 °C and slowly added to the reaction mixture.[7] The remaining acid chloride solution was added dropwise over 30 min, keeping the reaction temperature between −10 and −5 °C. After the addition was complete, the funnel was rinsed with THF (2 mL). H_2O (30 mL) was cooled to 0 °C and slowly added to the reaction mixture, maintaining the internal temperature below 0 °C. The entire mixture was poured into H_2SO_4 (20% aqueous solution, 25 mL) cooled to 0 °C. The resulting white suspension was extracted with Et_2O (2 × 50 mL). The combined ether layers were sequentially washed with H_2O (50 mL) and sodium phosphate buffer (pH 7.0, 50 mM, 3 × 50 mL). Drying ($MgSO_4$) and evaporation of the solvent in vacuo yielded peroxy acid (2.87 g, 85.5%) as a white powder (mp 85–87 °C) which was found to contain 99% active oxygen (iodometric titration): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.39–7.51 (m, 1 H), 7.58–7.67 (m, 1 H), 7.87–8.09 (m, 2 H); IR (Nujol) 3250, 1735, 1710, 1275, 1255, 1075, 900, 810, 730 cm^{-1}; MS, *m/e* (M$^+$, relative intensity) 172 ($C_7H_5{}^{35}Cl{}^{16}O_3$, 29), 174 ($C_7H_5{}^{37}Cl{}^{16}O_3$ and $C_7H_5{}^{35}Cl{}^{16}O_2{}^{18}O$, 45), 176 ($C_7H_5{}^{37}Cl{}^{16}O_2{}^{18}O$ and $C_7H_5{}^{35}Cl{}^{16}O{}^{18}O_2$, 22), 178 ($C_7H_5{}^{37}Cl{}^{16}O{}^{18}O_2$, 4); total active ^{18}O, 39%.

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Communications

Competition between Endocyclic and Exocyclic Periselectivity in Cycloadditions of *o*-Xylylenes to Fulvenes

Summary: The reactions of *o*-xylylenes with fulvenes produce [6 + 4], spiro [4 + 2], or ring [4 + 2] adducts, depending upon the substituents on the xylylene or fulvene.

Sir: We have described the propensity of "neutral" and electron-deficient dienes to cycloadd in a Diels–Alder ([4 + 2]) fashion to endocyclic double bonds of fulvenes.[1] On the basis of a consideration of the frontier molecular orbitals of fulvenes, we predicted,[1,2] and later found experimentally,[3,4] that electron-rich dienes undergo [6 + 4] cycloadditions to fulvenes. Padwa and co-workers found that a nitrile ylide undergoes both [6 + 4] and [4 + 2] cyclo-

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