p-dimethoxybenzene derivatives. We have found that ceric ammonium nitrate \([\text{Ce}({\text{NH}}_4)_2({\text{NO}_3})_3]\) in aqueous acetic acid may be inconvenient for large scale preparations. Both nitric acid and an effective base are required for the demethylation. Argentic oxide appears to be quite broad in its ability to perform this transformation. In addition to or instead of demethylation, argentic oxide also appears to be useful for the oxidation of quinone dimethyl ethers to quinones. This is the case for the oxidation of dimethoxybenzene derivatives, and especially noteworthy is the facile conversion of the benzyl alcohol 3a to the quinone 3b, since CAN has been reported to oxidize benzylalcohols to the corresponding benzaldehydes.4

Generally, good yields of \(p\)-benzoquinones were obtained from 2,5-disubstituted 1,4-dimethoxybenzene derivatives. With the monosubstituted derivative 2,5-dimethoxytoluene (8a), however, the major product was a dimer, 4,4'-dimethyl-2,5,2',5'-diquinone (8c),5 similar results were obtained with 1,2,4-trimethoxybenzene (9a). In the case of the completely unsubstituted \(p\)-dimethoxybenzene (1a) a moderate (57%) yield of benzoquinone (1b) was obtained. Apparently, the yield was reduced by competitive dimerization, although no attempt to characterize side products was made. As an example of napthoquinone formation, oxidation of 4a to 6a was achieved in nearly quantitative yield. Our success in the synthesis of \(o\)-quinones encouraged us to attempt to extend the reaction to the synthesis of \(o\)-quinones. Attempted oxidation of 1,2-dimethoxybenzene to \(o\)-benzoquinone was unsuccessful, presumably owing to oxidative coupling reactions and/or the instability of the product. On the assumption that bulky substituents might inhibit coupling reactions and stabilize the product, we carried out the oxidation of 3,5-di-tert-butyl-1,2-dimethoxybenzene (11a). This reaction produced the desired \(o\)-quinone 11b, as well as a second product, \(p\)-quinone 11c, which must result from cleavage of a tert-butyl group from the aromatic ring. This rather remarkable transformation can be rationalized in several ways. In the first place, it is a simple and efficient way of converting a sensitive material into a more stable one. In addition, it provides a convenient method for the preparation of \(o\)-quinones from \(p\)-quinones, which are often difficult to synthesize directly. Finally, it may have potential applications in the synthesis of other \(o\)-quinone derivatives, such as \(o\)-hydroxy- and \(o\)-amino-quinones.
by postulating the intermediary of carbinal 11d, which undergoes oxidation with loss of a tert-butyl group to give quinone 11e. It is well known that tertiary alcohols similar in structure to proposed intermediate 11d are cleaved to ketones by CAN.7

Although a detailed mechanistic study was beyond the scope of the present work, we felt that it would be worthwhile to determine whether the quinone formation involves alkyl- or aryl-oxygen bond cleavage. Oxidation of 1,4-dimethoxy-2,3,5,6-tetramethylbenzene (12a) in the presence of H$_2$O$_2$

\[
\begin{align*}
&\text{CH}_3\text{OCH}_2\text{CH}_3 + 2\text{CeO}_2^+ + 2\text{H}_2\text{O}^+ \\
&\rightarrow \text{CH}_3\text{OCH}_2\text{CH}_3 + 2\text{H}^+ + 2\text{Ce}^{4+} + \text{O}_2
\end{align*}
\]

(95% isotopic enrichment) provided doubly labeled duroquinone (12b) (90% isotopic enrichment by chemical ionization mass spectral analysis). A control experiment showed that duroquinone (12b) exchanges relatively slowly with H$_2$O$_2$ under the reaction conditions. Consequently, the oxidation must proceed by aryl-oxygen bond cleavage with the net formation of the quinone and 2 mol of methanol (eq 1). An identical mechanism has been established for analogous oxidations with argentate.*

The ready availability of CAN, the mild and convenient reaction conditions required, and the good to excellent yields obtained for a variety of compounds suggest that the reaction should find broad application.

**Experimental Section**

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. NMR spectra were recorded on a Varian A-60A or Perkin-Elmer R-12B instrument. Chemical shifts are reported in parts per million relative to Me$_4$Si as an internal standard. The uv spectra were recorded with a Nihonkoden spectrophotometer. The microanalytical data were performed by the Microanalytical Laboratory, University of California, Berkeley.

**General Procedure for Oxidative Demethylation.** Unless otherwise noted, the dimethoxy compound was dissolved in acetic anhydride to give 0.86 g of 1.15 mmol. The solution was stirred for 30 min at room temperature and then heated under reflux for 30 min. After cooling to room temperature the solution was poured into 50 ml of H$_2$O and extracted with ether (2 X 50 ml). The combined extracts were washed with H$_2$O (25 ml) and concentrated under reduced pressure to give 1.1 g of white solid, mp 116-120 °C. Recrystallization from ethanol-water gave 1.7 g (71%) of white needles: mp 124-125 °C; NMR (CDCl$_3$) $\delta$ 1.15 (t, $J = 1.5$ Hz, 3 H, CH$_3$), 2.86 (d, $J = 1.5$ Hz, 3 H, CH$_3$), 6.75 (d, $J = 6.5$ Hz, 2 H, CH$_2$), 3.82 (s, 6 H, OCH$_3$), 6.70 (s, 1 H, ArH).


1-(2-Dimethylamino-4-methylphenyl)-2-tert-butoxycarbonylaminopropane (6a).

A solution of 1-(2,4,5-trimethoxyphenyl)-2-benzamidopropane $\delta$ (1.38 g, 10 mmol) in acetonitrile (25 ml) was added to a solution of CAN (3.3 g, 6.0 mmol) to yield 1.97 g (6.0 mmol, 78%) of white needles: mp 72-74 °C; NMR (CDCl$_3$) $\delta$ 1.35 (d, $J = 1.5$ Hz, 3 H, CH$_3$), 2.76 (2 H, CH$_2$), 4.3-4.5 (1 H, CH) 6.0-6.5 (1 H, NH), 6.65 (2 H, C=CH); uv (H$_2$O) $\lambda_{max}$ 256 nm (e 16 800).

Anal. Calcd for C$_{16}$H$_{18}$N$_2$O: C, 65.14; H, 6.69; N, 4.53. Found: C, 65.14; H, 6.69; N, 4.53.

1-(2,5-Dimethyl-4-methylphenyl)-2-tetrahydroxybenzylaminopropane (6b).

A solution of CAN (1 g, 2.2 mmol) in 20 ml of H$_2$O was added to a solution of 6a (0.90 g, 1 mmol) in 50 ml of acetic anhydride over 3 min. After stirring for 15 min the deep yellow solution was diluted with 100 ml of H$_2$O which resulted in precipitation of the product. The precipitate was collected by filtration and air dried to give 0.74 g (76%) of 6b: mp 157-159 °C; NMR (CDCl$_3$) $\delta$ 1.35 (d, $J = 1.5$ Hz, 3 H, CH$_3$), 2.75 (2 H, CH$_2$), 4.3-4.5 (1 H, CH) 6.0-6.5 (1 H, NH), 6.70 (2 H, C=CH); uv (H$_2$O) $\lambda_{max}$ 260 nm (e 15 100).

Anal. Calcd for C$_{16}$H$_{18}$N$_2$O: C, 65.14; H, 6.69; N, 4.53. Found: C, 65.14; H, 6.69; N, 4.53.
Notes. Anal. Calcd for C_{12}H_{16}NO_2: C, 78.21; H, 5.73; N, 4.68. Found: C, 76.79; H, 5.78; N, 4.60.

Oxidation of 2,5-Dimethoxynaphthalene (9a). The oxidation of 9a (1.52 g, 10 mmol) with CAN (16.5 g, 50 mmol) was carried out in the usual manner. Sublimation of the crude product at 180 °C (30 mm) provided 0.1 g (0.8 mmol, 8%). 2-Methyl-1,4-benzoxazine (8b), mp 65-66.5 °C (lit. mp 64-65 °C). The pressure was reduced to 0.05 mm and 1.02 g (8.5 mmol, 85%) of the dimeric quinone 8c (mp 180-184 °C) was collected. Recrystallization from isopropyl alcohol–toluene gave pure 8c, mp 180-190 °C (lit. mp 180-190 °C).

Oxidation of 1,2,4-Trithiobenzene (9a). The reaction mixture of 9a (0.82 g, 5 mmol) with CAN (8.3 g, 15 mmol) was worked up by addition to ice water (100 ml) followed by filtration to collect the crude orange product 9e (0.2 g, 1.45 mmol, 29%), mp 225-227 °C (lit. mp 225-240 °C dec.).

1,4-Naphthoquinone (10b). Oxidation of 1,4-dimethoxy-1,2-naphthalene (10a, 1 g, 5.3 mmol) with CAN (8.8 g, 16 mmol) in the usual manner followed by sublimation (135 °C, 0.1 mm) of the crude product provided 0.79 g (4.98 mmol, 94%), mp 122.5-123.5 °C.

H+ Mass Spectra. CAN (0.48 mmol) and H_2O (0.1 g, 5.5 mmol, 95% 18O) were added to a small, oven-dried vial. 1,4-Dimethoxy-2,3,5,6-tetramethylbenzene (12a, 16.8 mg, 0.087 mmol) in 0.3 ml of dry acetonitrile was added, the vial was capped, and the mixture was shaken occasionally over a 15-min period. The upper (organic) layer was separated, the solvent was evaporated under reduced pressure, and the residue was sublimed (130 °C, 0.5 mm) to give 0.5 mg of yellow solid. Chemical ionization mass spectral analysis indicated 90% bias-1H-O-12b MH+ m/e (rel intensity) 169 (100), 167 (8.7), 165 (2.0). As a control, a solution of duroquinone (12b, 7.2 mg, 0.047 mmol) and 2,5-dimethyl-1,4-dihydrobenzene (2a, 14.2 mg, 0.085 mmol) in 0.4 ml of acetonitrile was treated with CAN (178 mg, 0.325 mmol) in H_2O (0.1 g, 5.5 mmol, 95% 18O). The quinones were isolated by sublimation and analyzed by chemical ionization mass spectrometry: MH+ m/e (rel intensity) 169 (19), 167 (54), 165 (100).

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Registry No.—1a, 150-73-7; 1b, 106-51-4; 2a, 2674-32-0; 2b, 157-18-8; 3a, 6009-82-8; 3b, 40970-52-8; 4a, 29907-72-0; 4b, 59963-56-9; 5a, 30784-23-7; 5b, 13573-57-0; 6a, 59963-38-1; 6b, 59963-39-2; 7a, 59963-60-5; 7b, 59963-61-6; 8a, 24596-58-4; 8b, 533-97-9; 8c, 4388-07-2; 9a, 135-77-3; 9c, 134023-37-1, 10a, 10075-72-0, 12a, 105-15-4; 11a, 22885-74-6, 1b, 3388-21-9, 11c, 2300-74-5; 12b, 527-17-3; CAN, 1674-21-3; 1-(2,5-dimethoxy-4-methylphenyl)-2-aminopropane, 15888953-1; tert-butoxycarbonyl azide, 1070-19-5; 1-(2,4-trimethyl-5-aminopropane hydrochloride, 159957-29-2; benzoyl chloride, 98-88-4.

References and Notes

(5) Argon ion oxidation of 2,5-dimethoxynapthalene also gives 8c as the major product.
(8) In contrast to duroquinone (12b), it was found that 2,5-dimethyl-1,4-benzoxazine (2b) and 1,4-naphthoquinone (10b) underwent relatively rapid exchange with H_2O. This finding is in accord with the results of Snyder and Rapoport that alkyl substitution adjacent to the carbonyl function greatly reduces the rate of 18O exchange in naphthoquinone derivatives.

A Regiospecific Synthesis of Functionalized Vinycyclopropanes via Cyclopropyl Cuprates

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The synthetic utility of the vinycyclopropane unit in the construction of cyclopendanes has been harped upon by the lack of mild, efficient, and regioselective routes to this class of compounds. One of the earliest approaches to vinycyclopropanes involved the addition of carbenes to dienes (route A).

\[
\text{[RC] + \text{E} \rightarrow \text{R} + \text{E}}
\]

This route usually suffers from lack of regioselectivity and generality. More recently, the addition of allyl ylides to Michael acceptors has provided a mild and efficient route to functionalized vinycyclopropanes (B); the recent work of Trost and co-workers also offers a number of solutions to the synthesis of vinycyclopropanes from cyclopentylithium reagents (C). In this report, we wish to report the facile construction of functionalized vinycyclopropanes utilizing the conjugate addition reactions of cyclopentylithium reagents to \(\alpha,\beta\)-unsaturated carbonyl compounds (D).