Novel Catalysis of Hydroquinone Autoxidation with Nitrogen Oxides

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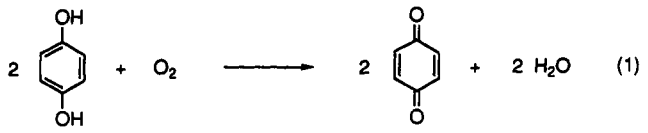
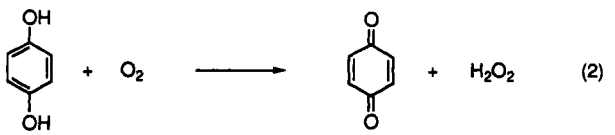
An efficient catalytic method is described for the preparative conversion of hydroquinones to quinones with dioxygen under mild conditions. The use of the gaseous nitrogen oxide (NO_x) catalyst allows a simple workup procedure for the isolation of quinones in essentially quantitative yields by merely removing the low-boiling solvent dichloromethane *in vacuo*. The mechanism of the catalytic autoxidation of hydroquinones is ascribed to the critical role of nitrosonium (NO^+) in the one-electron oxidation of hydroquinone, followed by the reoxidation of the reduced nitric oxide (NO) with dioxygen. An extensive series of complex interchanges among various NO_x species in nitrogen-(V), -(IV), -(III), and -(II) oxidation states, coupled with stepwise oxidation of hydroquinone *via* a successive series of one-electron/proton transfers, form the critical components of the catalytic cycle.

Introduction

The direct oxidation of hydroquinones with dioxygen is potentially a straightforward (four-electron) transformation to quinones, *i.e.*



In practice, it is beset by the inevitable interruption of the autoxidation at an intermediate (two-electron) stage,[1] *i.e.*



and the concomitant formation of hydrogen peroxide in eq 2 is commonly responsible for the myriad side products (humic acids, *etc.*) that most often accompany the preparation of different quinones.[2] Indeed, such a limitation is inherent to the free-radical chain process for aerial oxidations in general[3]—it is the basis for the commercial production of hydrogen peroxide.[4]

In this report, a novel catalytic method is presented for effecting the autoxidation of hydroquinones according to the *direct* stoichiometry in eq 1. Our discovery of the catalysis by nitrogen oxides enables the procedurally simple and efficient autoxidations to produce high preparative yields of quinones under mild conditions (temperature and nonpolar solvents).[5] In a more general context, the NO_x catalysis of autoxidation circumvents hydrogen peroxide as a deleterious byproduct, and it thus represents a viable alternative to conventional autoxidations *via* (alkyl)peroxy intermediates[6] of other types of electron-rich substrates.

Results

A suspension of hydroquinone in dichloromethane under an oxygen atmosphere remained essentially intact, even after prolonged stirring at room temperature. However, upon the addition of catalytic amounts of nitrogen dioxide, the slurry turned spontaneously into a clear (homogeneous) solution over the course of 1 day, and pure 1,4-benzoquinone was isolated in 94% yield. With this simple procedure, the various types of hydroquinones listed in Table 1 could be converted to the corresponding quinones in excellent yields (column 6). Moreover, the mild reaction conditions allowed the preparative transformation of hydroquinones to quinones to be selectively carried out in the presence of a remote double bond (see entry 12 in Table 1).[7]

In order to examine the nature of this interesting catalysis of autoxidation, we focused our attention primarily on hydroquinones **3**, **4**, and **9** owing to their high catalytic conversions as follows.

I. Catalytic Autoxidation of Hydroquinones with Nitrogen Oxides. A slurry of hydroquinone **3** (200 mmol) in dichloromethane (200 mL) was (magnetically) stirred at −10 °C under an oxygen atmosphere for several hours without perceptible change. When a small amount of nitrogen dioxide (2 mmol) was added, the suspension immediately took on a lemon-like coloration, and on continued stirring it yielded a clear pale yellow solution (~12 h). The simple removal of the solvent *in vacuo* led to quantitative yields of the crystalline quinone **3Q**, which upon spectral (NMR, IR, and GC–MS) analysis was found to be singularly free of organic impurities (<1%). The yield of quinone was thus in excess of 10 000% based on nitrogen dioxide as the added oxidant.[8]

The temporal requirement for the completion of the autoxidation varied with the amount of NO_2 added relative to the hydroquinone. Thus, the increasing time spans of 1, 3, 6, and 12 h were required for the quantitative conversion of the hydroquinone **9** when decreasing molar

• Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Horner, L. In *Autoxidation and Antioxidants*; Lundberg, W.O., Ed.; Interscience: New York, 1961; Vol. 1, pp 171ff.

(2) (a) Eller, W.; Koch, K. *Ber.* **1920**, *53*, 1469. (b) Eller, W.; Meyer, H.; Saenger, H. *Liebigs Ann. Chem.* **1923**, 431, 162, 177, and 133. (c) James, T. H.; Weissberger, A. *J. Am. Chem. Soc.* **1938**, *60*, 98, 2084.

(3) Denisov, E. T.; Mitskevich, N. I.; Agebekov, V. E. *Liquid Phase Oxidation of Oxygen-Containing Compounds*; Plenum: New York, 1977. See also: Bateman, L. *Quart. Rev. Chem. Soc.* **1954**, *8*, 147.

(4) *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed.; Interscience: New York, 1966; Vol. 11, pp 396ff.

(5) For a preliminary report, see: Rathore, R.; Bosch, E.; Kochi, J. K. *Tetrahedron Lett.*, in press.

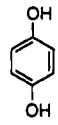
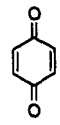
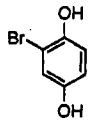
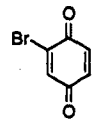
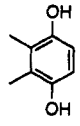
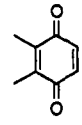
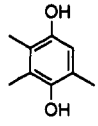
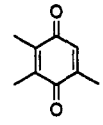
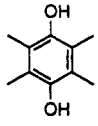
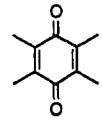
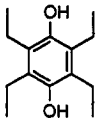
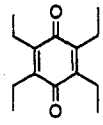
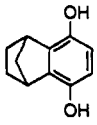
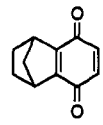
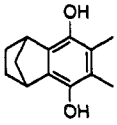
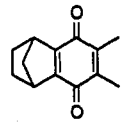
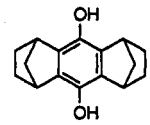
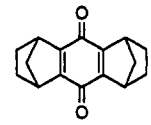
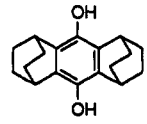
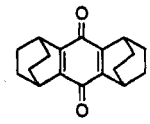
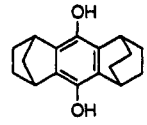
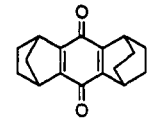
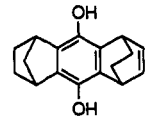
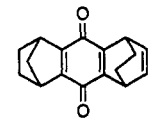
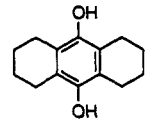
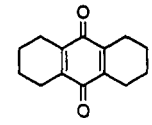
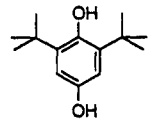
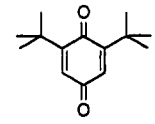
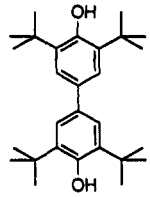
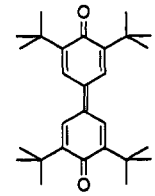
(6) Howard, J. A. *Adv. Free Radical Chem.* **1972**, *4*, 49.

(7) Preliminary experiments indicated that catechols are also effectively converted to *o*-quinones. (Rathore, R. Unpublished results).

(8) Brook, A. G. *J. Chem. Soc.* **1952**, 5040.

0022-3263/94/1959-2529$04.50/0

Table 1. Catalytic Autoxidation of Hydroquinones to Quinones

no.	hydroquinone (H_2Q)	(H_2Q)[a] (mmol)	NO_2[b] (M)	time[c] (h)	quinone (Q)	% yield[d]
1		50	0.04	20		94
2		20	0.10	10		99
3		200	0.01	12		100
4		180	0.01	10		100
5		50	0.04	6		100
6		20	0.10	2		100
7		200	0.01	10		99
8		50	0.04	3		100
9		100	0.02	12		98
10		100	0.02	18		98
11		20	0.10	2		98
12		15	0.13	2		99
13		40	0.05	4		97
14		100	0.02	8		100
15		50	0.04	4		98

[a] Dichloromethane (1 mL) was used for each mmol of H_2Q at −10 °C under an O_2 atmosphere (*e.g.*, 1 M solution of H_2Q in dichloromethane). [b] Concentration of added NO_2 (arbitrarily chosen to reflect reaction times) for various types of hydroquinones. [c] See text. [d] Isolated yields.

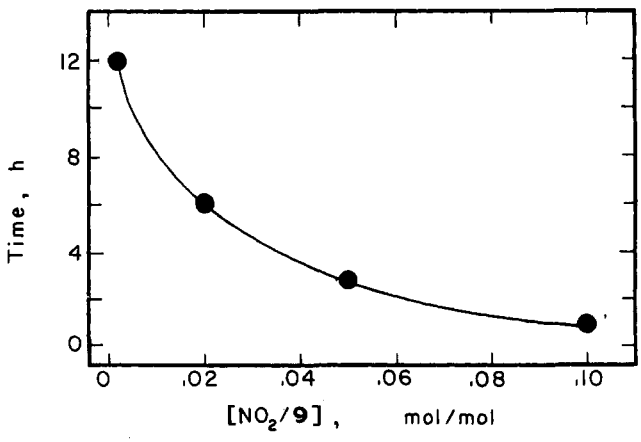
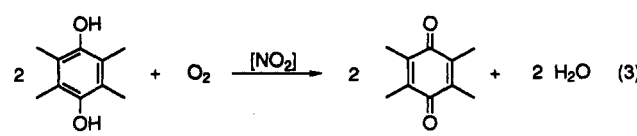


Figure 1. Rate dependence of the catalytic autoxidation of hydroquinone **9**, given by the time required for complete conversion (ordinate) as a function of the molar ratio of NO_2 to **9** (abscissa) in dichloromethane at −10 °C.

ratios of NO_2:**9** were present in dichloromethane under an O_2 atmosphere, as shown in Figure 1. This established the lower limit for the catalytic turnover to be at least 100 with respect to nitrogen dioxide. In order to quantify the dioxygen requirement, a suspension of hydroquinone **4** (5.87 mmol) in dichloromethane was treated with NO_2 (0.32 mmol) at −23 °C in a dry ice/CCl_4 bath, and the oxygen uptake was measured volumetrically with the aid of a gas buret. Cessation occurred when 66 mL (2.9 mmol) of dioxygen had been consumed (2 h), and the subsequent removal of solvent and nitrogen dioxide (gas) *in vacuo* led to crystalline quinone **4Q** in excellent yield (5.78 mmol) to establish the 2:1 stoichiometry in eq 3. Hydroquinone itself



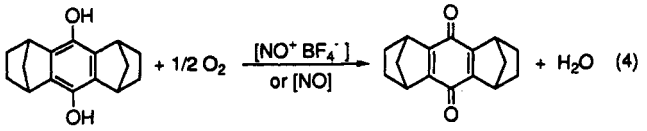
(3)

reacted somewhat slowly due to the separation of dark blue quinhydrone crystals[9] in the initial phases of the

(9) Patai, S., Ed. *The Chemistry of Quinonoid Compounds*; Wiley: New York, 1974; Part 1, pp 300, 314.

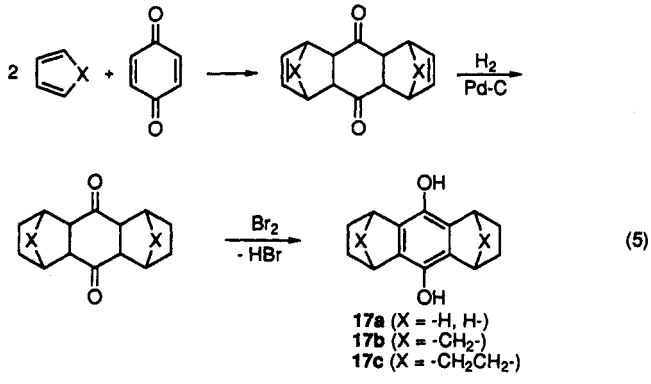
autoxidation. However, the continued stirring of the heterogeneous mixture at room temperature resulted in a clear yellow solution from which 1,4-benzoquinone was readily isolated in high yields.[10]

The catalytic autoxidation of hydroquinones could also be performed with small amounts of other nitrogen oxides such as nitrosonium salts ($NO^+BF_4^-$) or nitric oxide (NO). For example, the addition of a few crystals of $NO^+BF_4^-$ (~1 mol %) to a suspension of hydroquinone **9** in dichloromethane under an O_2 atmosphere led to an excellent yield of the quinone according to the stoichiometry in eq 4. The same results were obtained when the



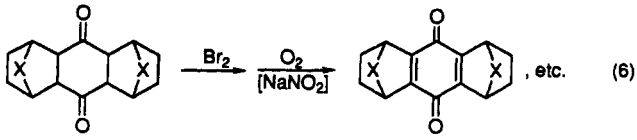
autoxidation was initiated by small amounts of nitric oxide.

The simplicity of these procedures prompted us to search for other, more convenient NO_x sources. Indeed, an inexpensive mixture of sodium nitrite and hydrochloric acid under an oxygen atmosphere was found to be an alternate source of NO_2. [Note that nitrous acid (resulting from nitrite neutralization) decomposed to dinitrogen trioxide,[11] which was then rapidly oxidized to nitrogen dioxide by dioxygen.[12]] Thus, the addition of a drop of hydrochloric acid (or acetic acid) to a heterogeneous mixture of **9** and sodium nitrite (1 mol %) in dichloromethane under an O_2 atmosphere (maintained by a gas-filled rubber balloon) led rapidly to the characteristic yellow suspension (*vide supra*). [The oxygen uptake was readily apparent from the rapid deflation of the balloon.] The clear yellow solution, after drying with anhydrous magnesium sulfate and filtration, was evaporated *in vacuo* to afford quinone **9** in excellent yield. This convenient procedure was readily applicable to the one-pot synthesis of quinones from the Diels–Alder ketones derived from the condensation of 1,4-benzoquinone with various dienes. For example, the Diels–Alder adducts are usually converted to the corresponding hydroquinones (**17a–c**) *via* bromination in chloroform followed by the removal of solvent and HBr according to eq 5.[13] However, the simple addition of sodium nitrite (5 mol %) under an O_2



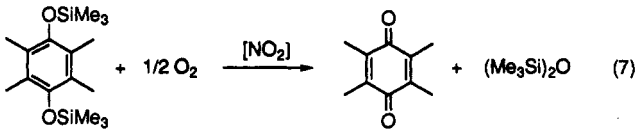
17a (X = -H, H-)
17b (X = $-CH_2-$)
17c (X = $-CH_2CH_2-$)

atmosphere at the end of the bromination step led to the direct conversion to quinones in high yields as illustrated in eq 6. Thus, the transformation in eq 6 represents a



"one-pot" procedure for the direct conversion of 1,4-cyclohexanediones to the corresponding quinones.

The limited solubility of the various hydroquinones in dichloromethane provided a convenient visual (temporal) probe, and it did not otherwise affect the course of autoxidation. Conversion of hydroquinones to their bis-(trimethylsilyl) ethers afforded a more soluble form in dichloromethane. It is thus noteworthy that a homogeneous solution of the bis(silyl) ether **16** of hydroquinone **9** was readily converted to **9Q** with catalytic amounts of NO_2 in the presence of dioxygen even at −10 °C. The



stoichiometry of the catalytic autoxidation in eq 7 was established by the separation and characterization of the volatile hexamethyldisiloxane in high yields (see Experimental Section).

II. Stoichiometric Oxidation of Hydroquinones with Nitrogen Oxide. The role of the nitrogen oxides in the catalytic autoxidation was examined by carrying out the direct oxidation of hydroquinones with stoichiometric amounts of NO_x under *anaerobic* conditions (argon atmosphere) as follows.

Nitrogen Dioxide Oxidation. When a slurry of hydroquinone **9** in dichloromethane under an argon atmosphere was treated with an equimolar amount of nitrogen dioxide at −78 °C, it yielded a transient blue-green mixture diagonistic of dinitrogen trioxide (λ_{max} = 685 nm, ϵ_{max} = 92 cm M^{-1})[14a] arising from the reversible equilibrium:[14]

$$NO + NO_2 \rightleftharpoons N_2O_3 \quad (8)$$

Upon continued stirring, the colored mixture faded and it was finally transformed into a clear yellow solution over which nitric oxide was sampled. Removal of the solvent *in vacuo* led to quantitative yields of quinone **9Q**. The NO in the head gas was characterized by the diagonistic nitrogen–oxygen stretching band at ν_{NO} = 1876 cm^{-1} in the IR spectrum[15] as well as the characteristic absorptions at λ_{max} = 204, 214, and 222 nm in the UV spectrum (see Figure 2A).[16] The introduction of dioxygen directly into the gas UV cell led to the absorption spectrum of nitrogen dioxide (Figure 2B),[17] which was clearly absent in Figure 2A, in accord with the 1:1 stoichiometry in eq 9. Further-

(10) The formation of quinhydrone may have led Brook[7] originally to believe that the oxidation with stoichiometric amounts of nitrogen dioxide was not applicable to hydroquinone.

(11) Markovits, G. Y.; Schwartz, S. E.; Newman, L. *Inorg. Chem.* **1981**, *20*, 445.

(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 320ff.

(13) Alder, K.; Stein, G. *Ann.* **1933**, *501*, 247.

(14) (a) Shaw, A. W.; Vosper, A. J. *J. Chem. Soc., Dalton Trans.* **1972**, 961. (b) Ashmore, P. G.; Tyler, B. J. *J. Chem. Soc.* **1961**, 1017. (c) Hisatsune, I. C.; Devlin, J. P.; Wada, Y. *J. Chem. Phys.* **1960**, *33*, 714.

(15) (a) Fateley, W. G.; Bent, H. A.; Crawford, B., Jr. *J. Chem. Phys.* **1959**, *31*, 204. (b) Keck, D. B.; Hause, C. D. *J. Mol. Spectrosc.* **1968**, *26*, 163. (c) Laane, J.; Ohlsen, J. R. *Prog. Inorg. Chem.* **1980**, *27*, 465.

(16) Marmo, F. F. *J. Opt. Soc. Am.* **1953**, *43*, 1186.

(17) Compare Hall, T. C., Jr.; Blacet, F. E. *J. Chem. Phys.* **1952**, *20*, 1745.

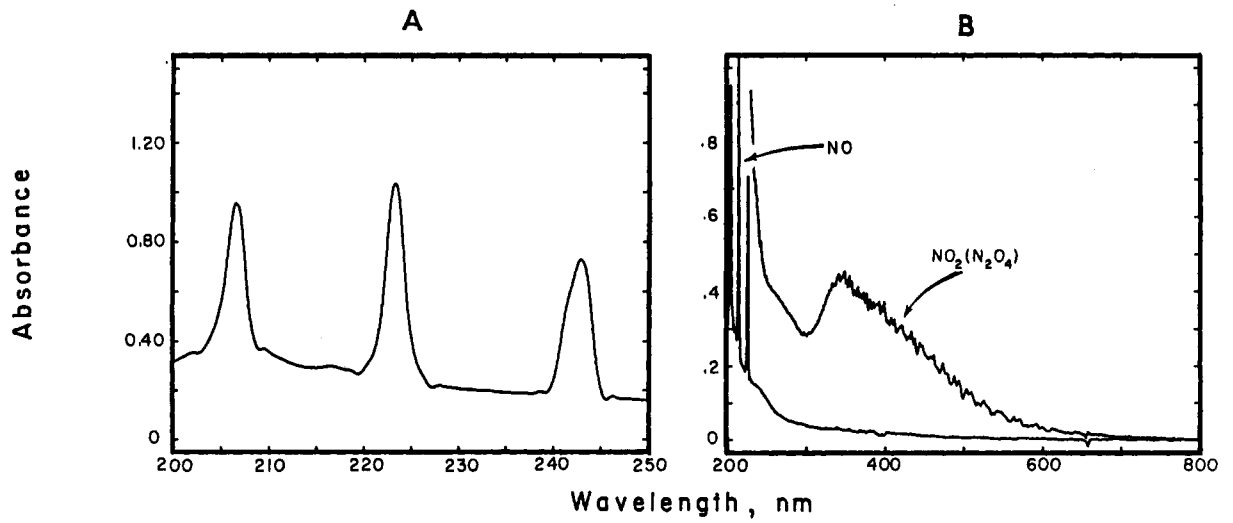
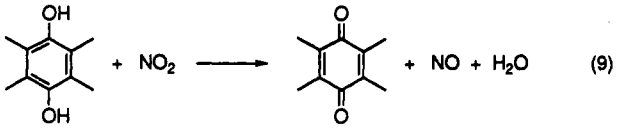
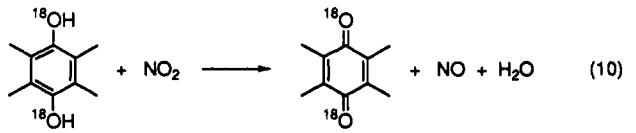


Figure 2. (A) The electronic spectrum of nitric oxide from the oxidation of hydroquinone **9** with an equimolar amount of nitrogen dioxide, showing the vibrational fine structure in the spectral region between 200 and 250 nm. [See (B lower) for the complete UV–vis spectrum between 200 and 800 nm.] (B) Absorption spectrum (upper) of nitrogen dioxide following the addition of dioxygen to A.

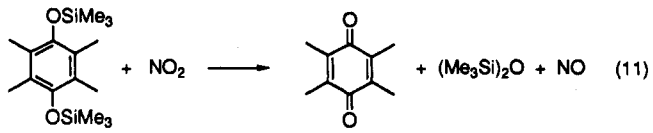


more, the treatment of hydroquinone **9** with a 0.5 equiv of NO_2 in dichloromethane under an argon atmosphere yielded only 0.5 equiv of **9Q**, and the remaining 0.5 equiv of **9** was recovered intact.

In order to ascertain the pathway by which hydroquinones was converted to quinones, a sample of doubly labeled [^{18}O]hydroquinone **9** was prepared *via* the oxidation of the dimethyl ether **18** of hydroquinone **9** with ceric ammonium nitrate in the presence of ^{18}O-labeled water,[18] followed by zinc-dust reduction. The oxidation of ^{18}O-labeled hydroquinone **9** with equimolar amounts of NO_2 was carried out in dichloromethane under an argon atmosphere, and quinone **9Q** was isolated in quantitative yields by the usual workup procedure. Mass spectral analysis indicated the complete retention of the ^{18}O labels in **9Q**, *i.e.*

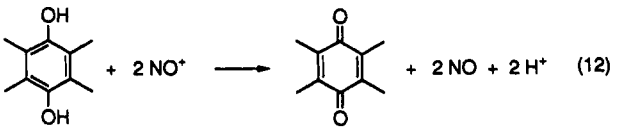


to clearly demonstrate that the quinone was derived *via* the oxidative scission of both oxygen–hydrogen (and not the oxygen–carbon) bonds of the hydroquinone. However, the presence of OH functionality was not a requirement since the silylated derivative was also quantitatively oxidized to the quinone **9Q** by equimolar amounts of NO_2 under the same reaction conditions, *i.e.*



The stoichiometry in eq 11 was confirmed by the spectral analysis of hexamethyldisiloxane and nitric oxide, as described in the Experimental Section.

Nitrosonium Oxidation. A mixture of hydroquinone **9** and 2 equiv of the nitrosonium salt $NO^+BF_4^-$ was prepared in a (O_2- and H_2O-free) glovebox and then slurried in dichloromethane at −78 °C under an argon atmosphere. Continued (magnetic) stirring of the heterogeneous mixture for 3 h yielded a dark yellow solution, which was allowed to warm to room temperature. The head gas was removed for spectral (UV, IR) analysis which indicated the presence of only nitric oxide. Neutralization of the dichloromethane solution with sodium bicarbonate, followed by filtration and evaporation, gave crystalline quinone **9Q** in 95% yield according to the stoichiometry in eq 12.



Discussion

The catalytic autoxidation of hydroquinones with nitrogen oxides according to the prototypical stoichiometry in eq 1 is unique in that there is no evidence for peroxidic intermediates that commonly accompany oxidations with O_2.[19] For a practical synthetic methodology, the ready removal of gaseous (NO_x) catalyst allows a trivial workup procedure for the isolation of pure quinones in essentially quantitative yields.[5] By contrast, the usual methods for the preparative conversion of hydroquinones to quinones require stoichiometric amounts of oxidants such as silver oxide, ceric ammonium nitrate, thallic nitrate, lead(IV) oxide, sodium dichromate, nitric acid, *etc.*[20–23] These are

(18) Jacob, P., III; Callery, P. S.; Shulgin, A. T.; Castagnoli, N., Jr. *J. Org. Chem.* **1976**, *41*, 3627.

(19) Mayo, F. R., Ed. *Oxidation of Organic Compounds*; Adv. Chem. Ser. 75–77, American Chemical Society: Washington, DC, 1968.

(20) (a) Fieser, L. F. *J. Am. Chem. Soc.* **1939**, *61*, 3467. (b) Ho, T. L.; Hall, T. W.; Wong, C. M. *Chem. Ind. (London)* **1972**, 729. (c) Fischer, A.; Henderson, G. N. *Synthesis* **1985**, 641.

(21) (a) Fischer, G. N. H. *Synthesis* **1985**, 64. (b) McKillop, A.; Perry, D. H.; Edwards, M.; Antus, S.; Farkas, L.; Nogradi, M.; Taylor, E. C. J. *Org. Chem.* **1976**, *41*, 282. (c) Jempty, T. C.; Gogins, K. A. Z.; Mazur, Y.; Miller, L. L. *J. Org. Chem.* **1981**, *46*, 4545.

(22) (a) Willstatter, R.; Parnas, J. *Ber.* **1907**, *40*, 282. (b) Vliet, E. B. *Organic Synthesis*; Wiley: New York, 1941; Collect. Vol. I, p 482.

either expensive reagents or are used in strongly acidic aqueous media and often require tedious workup and purification procedures.

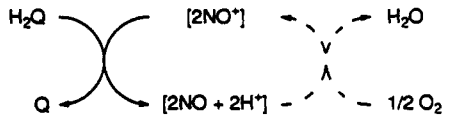
In order to gain insight into the nature of the catalytic autoxidation, we note that nitrogen oxides in three different oxidation states, *viz.* nitrogen(IV), -(III), and -(II) as NO_2, NO^+, and NO, respectively, can be employed with comparable catalytic efficiencies (compare eqs 3 and 4). Such an interchangeability among NO_x species is consistent with their ready interconversion during the course of a catalytic cycle. Although a rigorous kinetic study was precluded (owing to the limited solubility of hydroquinone in dichloromethane), the reactivity pattern illustrated in Figure 1 points initially to the direct oxidation of hydroquinone by nitrogen oxide. Accordingly, let us first focus on the redox changes that can occur with the various nitrogen oxides extant in the catalytic cycle.

Formally, the oxidation of hydroquinones (H_2Q) to quinones (Q) involves the removal of two electrons and two protons. This redox stoichiometry is established in eq 12 by the stoichiometric oxidation of hydroquinone to quinone with nitrosonium *via* a pair of one-electron reduction steps involving the transformation of nitrogen-(III) to -(II), *i.e.*

$$H_2Q + 2NO^+ \rightarrow Q + 2NO + 2H^+ \qquad (13)$$

This, together with the subsequent (re)oxidation of nitric oxide by dioxygen (which is known to be rapid[24]) can constitute the requisite reduction/oxidation for the catalytic autoxidation with NO^+, as described in eq 4. Accordingly, in Scheme 1, the solid arrows represent the stoichiometric reaction in eq 13, and the dashed arrows represent the schematic regeneration of NO^+ with dioxygen.

Scheme 1

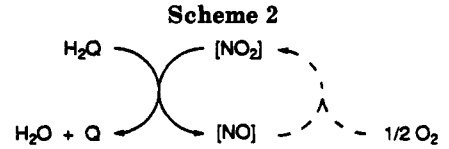


In a similar vein, the stoichiometric oxidation of hydroquinone with nitrogen dioxide (see eq 9) represents an alternative oxidation of hydroquinone via the two-electron reduction of nitrogen(IV) to -(II) in a single step, *i.e.*

$$H_2Q + NO_2 \rightarrow Q + NO + H_2O \qquad (14)$$

This, together with the subsequent (re)oxidation of nitric oxide with dioxygen constitutes the reduction/oxidation cycle in Scheme 2 for the catalytic autoxidation with NO_2, as described in eq 3. (The solid and dashed arrows have the significance described above.)

Scheme 2



(23) (a) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963**, 3028. (b) Durst, H. D.; Mack, M. P.; Wudl, F. *J. Org. Chem.* **1975**, *40*, 268.

(24) Smith, J. H. *J. Am. Chem. Soc.* **1943**, *65*, 74.

The two catalytic cycles presented schematically in Schemes 1 and 2, while seemingly disparate, are merged into a single unified mechanism by the ready interconversion of NO^+ and NO_2. Thus, the reversible dimerization of NO_2 to the nitro–nitro dimer is known to be accompanied by the isomeric nitrito–nitro dimer, *i.e.*[25,26]

$$O_2N\text{–}NO_2 \rightleftharpoons 2NO_2 \rightleftharpoons ONO\text{–}NO_2 \qquad (15)$$

Significantly, the nitrito dimer in eq 15 has been shown to afford the nitrosonium ion pair $NO^+NO_3^-$ which is tantamount to the disproportionation of nitrogen dioxide.[27] Although such a heterolysis of the N–O bond is unlikely to be important in nonpolar media such as dichloromethane, we recently showed how the complexation of the nitrosonium moiety by an aromatic donor (ArH) can promote ion-pair formation by several orders of magnitude, *i.e.*[28]

$$ONO\text{–}NO_2 \rightleftharpoons NO^+NO_3^- \overset{ArH}{\rightleftharpoons} [ArH,NO^+]NO_3^- \qquad (16)$$

On the basis of the understanding of the interaction of nitrosonium with aromatic donors,[29] hydroquinones are expected to strongly shift the equilibria in eq 16 to favor disproportionation in measure with their enhanced donor properties.[30] Accordingly, we propose that the oxidation of hydroquinone with nitrogen dioxide proceeds *via* the disproportionated ion pair, nitrosonium nitrate. Thus, 2 equiv of nitrosonium nitrate are converted to 2 equiv each of nitric acid and nitric oxide according to the stoichiometry embodied in eq 12. This mixture of nitrogen oxides is metastable, and it is rapidly converted to dinitrogen trioxide and dinitrogen tetraoxide with the liberation of water, *i.e.*[31,32]

$$2HNO_3 + 2NO \underset{-H_2O}{\rightarrow} N_2O_3 + N_2O_4 \qquad (17)$$

Since dinitrogen trioxide is in mobile equilibrium with NO and NO_2,[33] it is readily converted to N_2O_4 (NO_2) with dioxygen. As such, the more detailed catalytic cycle for the NO_2 catalysis of hydroquinone autoxidation can be readily presented as Scheme 3.[34]

The complex equilibria amongst the various nitrogen oxides in Scheme 3 underscores the multiple precursors that can be gainfully employed to initiate the catalytic

(25) (a) Brunning, J.; Frost, M. J.; Smith, I. W. M. *Int. J. Chem. Kinet.* **1988**, *20*, 957. (b) Redmond, T. F.; Wayland, B. B. *J. Phys. Chem.* **1968**, *72*, 1626. (c) Vosper, A. J. *J. Chem. Soc. A* **1970**, 2191. (d) James, D. W.; Marshall, R. C. *J. Phys. Chem.* **1968**, *72*, 2963.

(26) Pinnick, D. A.; Agnew, S. F.; Swanson, B. I. *J. Phys. Chem.* **1992**, *96*, 7092.

(27) (a) Parts, L.; Miller, J. T., Jr. *J. Chem. Phys.* **1965**, *43*, 136. (b) Bontempelli, G.; Mazzocchin, G.-A.; Magno, F. *Electroanal. Chem. Interfac. Electrochem.* **1974**, *55*, 91. (c) Wartel, M.; Boughriet, A.; Fischer, J. C. *Anal. Chim. Acta* **1979**, *110*, 211.

(28) Bosch, E.; Kochi, J. K. *Res. Chem. Intermed.* **1993**, *16*, 811.

(29) Kim, E. K.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 4962.

(30) See: Hammerich, O.; Svensmark, B. In *Organic Electrochemistry*, 3rd ed.; Lund, H., Baizer, M. M., Eds.; Dekker: New York, 1990; pp 615ff.

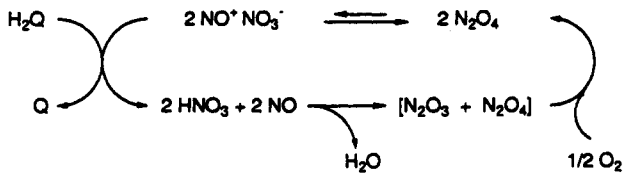
(31) (a) Forsythe, W. R.; Giauque, W. F. *J. Am. Chem. Soc.* **1942**, *64*, 48. (b) Boughriet, A.; Fischer, J. C.; Leman, G.; Wartel, M. *Bull. Soc. Chim. Fr.* **1985**, I-8.

(32) For the redox process in eq 17 under reaction conditions, see Experimental Section. This probably proceeds *via* a prior oxygen-atom transfer from nitric acid to NO, followed by the known decomposition of nitrous acid to dinitrogen trioxide and water.[11]

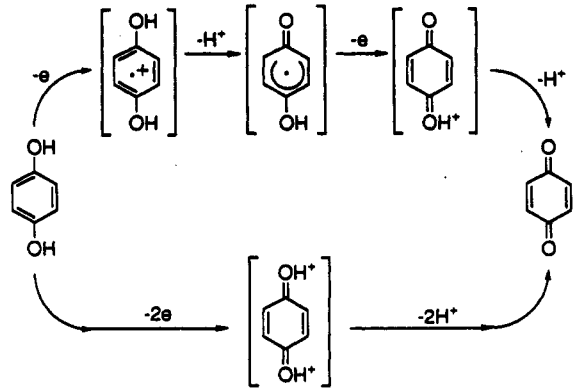
(33) Beattie, I. R.; Bell, S. W. *J. Chem. Soc.* **1957**, 1681.

(34) (a) Note that presence of H_2Q is implied in the disproportionation of N_2O_4 (see eq 16). (b) Some NO^+ may also be regenerated (together with nitrous acid) *via* the acid-induced ionization of N_2O_3 (compare: Boughriet, A. and Wartel, M. *J. Chem. Soc., Chem. Commun.* **1989**, 809.

Scheme 3



Scheme 4



autoxidations. Of utmost importance to the actual oxidation of hydroquinones, however, is the oxidation with NO^+ in eq 13—the other nitrogen oxides being primarily pertinent to the reoxidation part of the catalytic cycle. The overall two-electron oxidation of hydroquinone to quinone by 2 equiv of NO^+ most likely proceeds *via* successive one-electron steps. If so, the ^{18}O labeling studies in eq 10 show that it occurs by scission of both oxygen–hydrogen bonds.[35] In the one-electron mechanism illustrated in Scheme 4,[36] the hydroquinone cation radical ($H_2Q^{\bullet+}$) is the obligatory intermediate.[29]

However, the hydroquinone cation radical is a highly transient species and undergoes rapid deprotonation, being spectrally observed only in strongly acid media.[37] Thus, our attempts to detect independently the radical cation $9^{\bullet+}$ by quenching the photoexcited chloranil (CA) triplet with **9** to produce the radical ion pair[38] [$9^{\bullet+}$, $CA^{\bullet-}$] were unsuccessful. Indeed, our ability to spectrally observe only the hydrochloranil radical ($CAH^{\bullet}$) at the shortest time resolution following the application of the 10-ns laser pulse clearly indicated that the lifetime of $9^{\bullet+}$ was less than 10^{-10} s owing to its rapid proton transfer to the counterion ($CA^{\bullet-}$).[39] Transient (anodic) electrochemical studies also failed to detect hydroquinone radical cations,[38,40] except in highly acidic media.[37] Although the alternative to the one-electron mechanism for hydroquinone oxidation in Scheme 4 cannot be ruled out,[41] we note that most of the reagents which have been employed in the preparative conversion of hydroquinones to quinones, *e.g.*, silver(II) oxide, iron(III) chloride, cerium(IV) nitrate, etc., are one-electron oxidants,[20-22] for which the electron-transfer pathway seems to be the most reasonable. In such a process, the catalytic efficiency depends on (a) the effective electron transfer from the hydroquinone (H_2Q) to NO^+ and (b) the rapid followup step of the hydroquinone cation radical ($H_2Q^{\bullet+}$) to suffer rapid proton loss. The driving force for the electron transfer, *i.e.*

$$H_2Q + NO^+ \rightarrow H_2Q^{\bullet+} + NO \qquad (18)$$

is estimated to be exergonic by roughly $\Delta G \simeq -5$ kcal mol^{-1}, based on $E_{ox}^0 = 1.3$ V vs SCE for hydroquinone[37] and $E_{red}^0 = 1.5$ V vs SCE for nitrosonium[42] in dichloromethane. Such a moderate exergonic driving force for electron transfer coupled with the short lifetime of the $H_2Q^{\bullet+}$ ($\tau < 10^{-10}$ s) is sufficient to promote hydroquinone oxidations with NO^+—certainly at rates consistent with the catalytic turnovers observed in Table 1. Basically, the same conclusion applies to the facile catalytic autoxidation in eq 7 of the bis(trimethylsilyl) ether of hydroquinone **9** *via* the stoichiometric process outlined in eq 11 (with $2NO_2 \rightarrow NO^+NO_3^-$). Thus, electrochemical studies have confirmed the enhanced donor properties of hydroquinone silyl ethers (like those of the parent hydroquinones),[43] and time-resolved spectroscopy has established the exceptionally labile character of the trimethylsilyl group in aromatic cation radicals.[44]

Summary and Conclusions

The oxidation of various hydroquinones (H_2Q) to quinones (Q) in very high yields is rapidly effected with dioxygen and catalytic amounts of nitrogen oxide (NO_x) at room temperature or below. The catalytic cycle for autoxidation is deduced from the facile oxidation of H_2Q at −78 °C with stoichiometric amounts of the 1-electron oxidant, nitrosonium—either as the simple salt $NO^+BF_4^-$ or the disproportionated ion pair $NO^+NO_3^-$ derived from nitrogen dioxide.[28] The regeneration of NO^+ occurs by the subsequent oxidation of nitric oxide (NO) with dioxygen to nitrogen dioxide followed by the disproportionation in eq 16. The ready interconversion of the different nitrogen oxides ($NO_x = NO_2$, NO^+, and NO) in the catalytic cycle (Scheme 3) is then coupled to the hydroquinone oxidation in successive one-electron steps *via* the transient hydroquinone cation radical ($H_2Q^{\bullet+}$) in Scheme 4. The simple preparative procedure for the catalytic autoxidation of hydroquinones thus belies the complex series of facile interchanges of NO_x species that underlie the catalytic cycle. In a more general biochemical context, a reviewer has suggested that this catalytic study may provide a link between NO-associated biological species and quinone pathways.[45]

Experimental Section

Materials. Nitrosonium tetrafluoroborate ($NO^+BF_4^-$) (Pfaltz and Bauer) was stored in a Vacuum Atmosphere HE-493 drybox free from traces of oxygen, moisture, and solvent vapors. Nitrogen

(35) In contrast to the scission of the aryl–oxygen bond in hydroquinone dimethyl ethers. See: Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1972**, *94*, 227. Jacob *et al.* in ref 18.
(36) Parker, V. D. *Electrochim. Acta* **1973**, *18*, 519.
(37) Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1982**, *B36*, 63.
(38) Compare: Gschwind, R.; Haselbach, E. *Helv. Chim. Acta* **1979**, *62*, 944. Bockman, T. M.; Perrier, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 595.
(39) Hubig, S. M., unpublished results.
(40) (a) Eggins, B. R.; Chambers, J. Q. *J. Chem. Soc., Chem. Commun.* **1969**, 232. (b) Eggins, B. R.; Chambers, J. Q. *J. Electrochem. Soc.* **1970**, *117*, 186.
(41) Thus, nitric acid[23a] and *N*-chlorosuccinimide[23b] are not commonly believed to be one-electron oxidants.
(42) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196.
(43) Stewart, R. F.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 4999.
(44) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973.
(45) Feldman, P. L.; Griffith, O. W.; Stuehr, D. J. *Chem. Eng. News* **1993**, Dec. 20, 26.

dioxide (Aldrich) was purified according to Addison.[46,47] Sodium nitrite (Aldrich) was used without further purification. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of concd sulfuric acid (~20% by volume) until the acid layer remained clear. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride. Dichloromethane was dried over anhydrous calcium chloride and distilled twice from P_2O_5 under an argon atmosphere. It was stored in a Schlenk tube equipped with a Teflon valve fitted with Viton O-rings. Dry, deoxygenated dichloromethane was used in this study to avoid the effect of adventitious impurities, particularly on the determination of the stoichiometry of oxidation of hydroquinones with nitrogen oxides. For synthetic preparations, reagent-grade dichloromethane may be used without purification.

Hydroquinones 1–4 (Aldrich) were used without further purification. Hydroquinones 5, 14, and 15 were prepared from the corresponding quinones (Aldrich) by Zn-dust reduction in acetic acid.[48] Hydroquinones 6,[49] 7,[50] 8,[51] 9,[13] 10,[13] 11,[13] and 13,[13] and diketones 17a–c[13] were prepared according to the literature procedures. Hydroquinone 12 was obtained by the condensation of quinone 7Q with cyclohexadiene, followed by aromatization with Br_2 according to Paquette and co-workers.[52]

Instrumentation. The ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 NMR spectrometer, and the chemical shifts are reported in parts per million downfield from tetramethylsilane. Infrared spectra were recorded on a Nicolet 10DX FT-IR spectrometer. The UV–vis absorption spectra were measured on a Hewlett-Packard 8450A diode-array spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5790A chromatograph equipped with a flame ionization detector, using a 12.5-m SE-30 capillary column. The GC–MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP5970 mass spectrometer.

Catalytic Oxidation of Hydroquinones Using NO_2. General Procedure. Hydroquinone 9 (24.2 g, 100 mmol) was suspended in dichloromethane (95 mL) in a 250-mL flask equipped with a side arm. The flask was purged with O_2 and stoppered with a rubber septum, and the side arm of the flask was attached to an O_2-filled balloon in order to maintain the oxygen atmosphere. The mixture was cooled in an ice–acetone bath (approximately −10 °C), and a solution of NO_2 in dichloromethane (5 mL, 0.2 M) was added with the aid of a hypodermic syringe. The reaction mixture was stirred until the slurry yielded a clear yellow solution (12 h). The solvent was then evaporated *in vacuo* to afford crystalline quinone 9Q which upon GC and NMR analysis was found to be free of organic impurities (<1%).

Measurement of Oxygen Uptake. 2,3,5-Trimethylhydroquinone (4) (0.892 g, 5.87 mmol) was added under a flow of oxygen to a dichloromethane (20 mL) solution of NO_2 (0.32 mmol) cooled to −23 °C in a constant temperature dry ice/CCl_4 bath. The flask was immediately connected to a pressure-equalized gas buret filled with dioxygen. The temperature was carefully maintained at −23 °C and the slurry stirred while the oxygen uptake was monitored. After 2 h, 66 mL of oxygen (2.94 mmol) was consumed and the uptake of oxygen ceased. The dichloromethane solution was decanted and the solvent removed *in vacuo*. The residue consisted of pure 2,3,5-trimethylbenzoquinone (0.867 g, 5.78 mmol). A portion of the water which formed during the reaction, remained in the flask, and was weighed (49 mg, 2.7 mmol).

Catalytic Oxidation of Hydroquinone 9 Using $NO^+BF_4^-$. In a typical procedure, a flask was charged with nitrosonium tetrafluoroborate (52 mg, 0.44 mmol) in a drybox. Dichloromethane (10 mL) was added under an oxygen atmosphere, and an O_2-filled balloon was attached to the side arm of the flask. (The nitrosonium salt was not soluble in dichloromethane.) To the above mixture was added hydroquinone 9 (930 mg, 3.78 mmol) and the reaction mixture stirred overnight at room temperature to yield a clear yellow solution. The solution was diluted with dichloromethane (50 mL), washed with water, and dried over $MgSO_4$. Evaporation of the solvent gave quinone 9Q (905 mg, 100%) by GC–MS and NMR analysis.

Catalytic Oxidation of Hydroquinone 9 Using Nitric Oxide (NO). A suspension of hydroquinone 9 (12.1 g, 50 mmol) in dichloromethane (50 mL) was purged with dioxygen, and an O_2-filled balloon was attached to the side arm of the flask. The suspension was cooled in an ice–acetone bath, and 20 mL of NO (gas) was injected directly into the suspension with the aid of a hypodermic syringe. The characteristic yellow color was observed immediately. The reaction mixture was stirred overnight (~12 h) to yield a clear yellow solution which was dried over $MgSO_4$. Evaporation of the solvent *in vacuo* gave crystalline quinone 9Q (11.7 g, 98%).

Catalytic Oxidation of Hydroquinones Using Sodium Nitrite/Hydrochloric Acid. General Procedure. Hydroquinone 9 (24.4 g, 100 mmol) and sodium nitrite (345 mg, 5 mmol) were suspended in dichloromethane (100 mL) in 250-mL flask equipped with a side arm. The flask was purged with O_2 and stoppered with a rubber septum and an O_2-filled balloon attached to the side arm. The flask was cooled in an ice–acetone bath (approximately −10 °C), and 1 drop of concentrated hydrochloric acid added. The reaction mixture was stirred for 3 h, at which time a clear yellow solution was obtained. It was dried over $MgSO_4$ and filtered; the removal of solvent gave quinone 9Q in quantitative yield (24 g).

One-Pot Synthesis of Quinone from 1,4-Diketone. General Procedure. Dodecahydro-1,4:5,8-dimethano-9,10-anthraquinone (17b) (24.4 g, 100 mmol) was dissolved in chloroform (100 mL) at room temperature and a solution of Br_2 (16.0 g, 100 mmol) in chloroform (100 mL) added dropwise over 0.5 h under an argon atmosphere. The resulting suspension was stirred at room temperature for 3 h. Most of the HBr produced in the reaction was blown off by bubbling oxygen through the reaction mixture. The resultant suspension was cooled in an ice–acetone bath, and an O_2-filled balloon was attached to the side arm of the flask. Solid sodium nitrite (345 mg, 5 mmol) was then added to the reaction mixture, and after 3 h of stirring a clear yellow solution was obtained. It was dried over magnesium sulfate, and evaporation of the solvent *in vacuo* afforded quinone 9Q in 98% yield (23.5 g).

Catalytic Oxidation of the Bis(silyl) Ether 16 of Hydroquinone 9 with NO_2. Preparation of the Bis(silyl) Ether 16. To a stirred solution of hydroquinone 9 (12.1 g, 50 mmol) in dry acetonitrile (200 mL) were added trimethylsilyl chloride (12 g, 110 mmol) and hexamethyldisilazane (19.4 g, 120 mmol) successively. The reaction mixture was stirred overnight, and the usual workup[43] gave the bis(silyl) ether 16 (18.5 g, 96%): ^1H NMR ($CDCl_3$) δ 0.20 (s, 18H), 1.07 (sym m, 4H), 1.35 (sym m, 2H), 1.55 (sym m, 2H), 1.70 (sym m, 4H), 3.36 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 0.58, 26.74, 40.88, 48.79, 136.56, 148.95; GC–MS M^+ 386.

Catalytic Oxidation of 16. A solution of the bis(silyl) ether 16 (3.86 g, 10 mmol) in dichloromethane (10 mL) was cooled in an ice–acetone bath under an oxygen atmosphere. The oxygen atmosphere was maintained by an O_2-filled balloon attached to the side arm of the flask. A solution of NO_2 in dichloromethane (1 mL, 0.2 M) was added to the reaction mixture, which became progressively deeper yellow with time. It was periodically analyzed by GC. On complete dissolution (12 h) the solvent was removed *in vacuo* to afford crystalline 9Q (2.38 g, 99%). The volatile fraction was trapped with a cold finger that was cooled with a dry ice–acetone bath. From the cold trap, dichloromethane was carefully removed in order to isolate hexamethyldisiloxane (1.05 g, 72%) which was characterized by GC–MS and NMR analysis by comparison to an authentic sample (Aldrich).

Stoichiometric Reaction of Hydroquinone with NO_2. General Procedure. Hydroquinone 9 (97 mg, 0.4 mmol) was added under an argon atmosphere to a 1-cm quartz cuvette equipped with a side arm and Teflon needle valve (Schlenk

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adapter). The cuvette was cooled in a dry ice–acetone bath (approximately −78 °C), and a cooled solution of NO_2 in dichloromethane (2 mL, 0.2 M) was added under an argon atmosphere. The color of the reaction mixture changed from blue-green to yellow upon warming to room temperature (~5 min), and a clear solution was finally obtained. The gases from the cuvette were then transferred to an evacuated gas-phase IR cell (5-cm path length); the IR spectrum showed a characteristic sharp band at 1875 cm^{-1} and a pair of broad bands centered at 1845 and 1906 cm^{-1} characteristic of the P, Q, and R branches of nitric oxide (NO). The gases from the IR cell were then transferred to an evacuated 1-cm quartz cuvette and the UV absorption spectrum of the gases recorded. Three sharp absorption bands at 204, 214, and 226 nm were observed (see Figure 2a) and found to be identical to the spectrum recorded from authentic (purified) NO. Importantly, both UV and IR spectra showed no NO_2. Removal of the solvent on a rotary evaporator gave crystalline quinone **9Q** (96 mg, 100%) which was analyzed by GC, GC–MS, and NMR.

Reaction of Hydroquinone 9 with $NO^+BF_4^-$. A Schlenk flask was charged with nitrosonium tetrafluoroborate (117 mg, 1 mmol) in the drybox, and dichloromethane (20 mL) was then added under an argon atmosphere with the aid of a hypodermic syringe. (Note that NO^+ salt is not soluble in dichloromethane.) The slurry was cooled in a dry ice–acetone bath (approximately −78 °C), and hydroquinone **9** (121 mg, 0.5 mmol) was added. The reaction mixture was stirred for 3 h at which time a dark yellow solution was obtained. The gases were removed, and UV and IR analyses indicated the presence of only nitric oxide (NO). Sodium bicarbonate was added to the dichloromethane solution. After filtration and evaporation of the solvent, it gave quinone (115 mg, 95%) by GC–MS and NMR analysis.

Reaction of Bis(trimethylsilyl) Ether (16) of Hydroquinone 9 with NO_2. The silyl ether **16** (154 mg, 0.4 mmol) and a solution of NO_2 (2 mL, 0.2 M) were similarly treated at −78 °C under an argon atmosphere. Gaseous NO and quinone (95 mg, 99%) were characterized as described above, and hexamethyldisiloxane was compared with an authentic sample (GC, GC–MS, and NMR).

Oxidation of ^{18}O-Labeled Hydroquinone 9 Using NO_2. Preparation of ^{18}O-Labeled Hydroquinone 9. The dimethyl ether **18** of hydroquinone **9** (189 mg, 0.7 mmol) was dissolved in dry acetonitrile (3 mL), and a solution of ceric ammonium nitrate (1.54 g, 2.8 mmol) in $H_2{}^{18}O$ (95% ^{18}O enriched, 1 g) was added all at once. The reaction mixture was left at room temperature for 10 min, after which the doubly labeled quinone **9** (166 mg, 97%) was isolated according to the literature procedure[18] (GC–MS: M^+ 244). To a yellow solution of labeled **9** (H_2Q) (100 mg, 0.41 mmol) in acetic acid (5 mL) was added zinc dust (3–4 g), and the mixture heated for 2 min to yield a clear solution which was quickly filtered and cooled in an ice bath. The crystalline labeled **9** (H_2Q) was filtered and dried *in vacuo* (94 mg, 93%).

Oxidation of Isotopically Labeled Hydroquinone 9 with NO_2. By use of the general procedure described above, ^{18}O-labeled hydroquinone **9** (24.6 mg, 0.1 mmol) was treated with NO_2 in dichloromethane (1 mL, 0.1 M) that was prechilled to −78 °C under an argon atmosphere. Removal of solvent *in vacuo* gave pure quinone **9Q** (24 mg, 100%, GC–MS M^+ 244). (Note that with GC–MS analysis the ^{16}O quinone **9Q** showed M^+ 240.)

The quinones listed in the Table 1 were found to be identical to commercial samples or to authentic samples prepared by literature procedures. The characteristic data are as follows. 1,4-Benzoquinone (**1**): mp 112–114 °C (Aldrich). 2-Bromo-1,4-benzoquinone (**2**): mp 162–163 °C (Aldrich). 2,3-Dimethyl-1,4-benzoquinone[52] (**3**): mp 56–57 °C; ^1H NMR ($CDCl_3$) δ 1.96 (s, 6H), 6.66 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 12.07, 136.13, 140.92, 187.30. 2,3,6-Trimethyl-1,4-benzoquinone[53] (**4**): mp 31–32 °C; ^1H NMR ($CDCl_3$) δ 1.88 (s, 3H), 1.90 (s, 3H), 1.92 (d, 3H, J = 1.5 Hz), 6.43 (q, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 11.84, 12.14, 15.67, 132.83, 140.50, 140.66, 145.11, 187.21, 187.59. Duroquinone (**5**): mp 110–112 °C (Aldrich). Tetraethyl-1,4-benzoquinone[55] (**6**): mp 54–55 °C; IR (KBr) 2973, 2938, 2879, 1642 (vs), 1613, 1460, 1329, 1291, 1254, 1236, 1060, 1052, 962, 841, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, 12H, J = 7.5 Hz), 2.42 (q, 8H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ13.95, 19.63, 144.97, 187.50; GC–MS M^+ 220. 1,4-Methano-1,2,3,4-tetrahydro-5,8-naphthoquinone[50] (**7**): mp 39–40 °C; ^1H NMR ($CDCl_3$) δ 1.01 (sym m, 2H), 1.26 (d, 1H, J = 8.7 Hz), 1.48 (d, 1H, J = 8.7 Hz), 3.31 (br s, 2H), 6.64 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 24.63, 40.26, 47.45, 135.83, 151.12, 184.02; GC–MS M^+ 174. 1,4-Methano-1,2,3,4-tetrahydro-6,7-dimethyl-5,8-naphthoquinone[51] (**8**): mp 68–70 °C; IR (KBr) 2997, 2973, 2950, 2873, 1642 (vs), 1595, 1451, 1376, 1334, 1290, 1273, 1224, 1109, 947, 784 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (sym m, 2H), 1.30 (d, 1H), 1.53 (sym m, 1H), 1.83 (sym m, 2H), 1.92 (s, 6H), 3.41 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 12.05, 25.06, 40.68, 47.34, 139.95, 150.97, 184.51; GC–MS M^+ 202. 1,4:5,8-Dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone[13] (**9**): mp (sublimes at 200–230 °C); IR (KBr) 2995, 2971, 2952, 2875, 1648 (vs), 1638 (s), 1569, 1330, 1272, 1210, 1119, 875, 760, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (br d, 4H), 1.34 (d, 2H, J = 8.7 Hz), 1.57 (d, 2H, J = 8.7 Hz), 1.86 (br d, 4H), 3.42 (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 24.79, 40.19, 48.08, 150.97, 181.97; GC–MS M^+ 240. 1,4:5,8-Diethano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone[13] (**10**): mp (sublimes at 280–340 °C); IR (KBr) 2959, 2947, 2913, 2870, 1648 (vs), 1692, 1597, 1356, 1304, 1238, 1146, 818, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (d, 8H, J = 7.5 Hz), 1.68 (d, 8H, J = 7.5 Hz), 3.32 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 25.28, 26.34, 147.24, 187.40; GC–MS M^+ 268. 1,4-Ethano-5,8-methano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone[13] (**11**): mp (sublimes at 220–240 °C); IR (KBr) 2951, 2869, 1643 (vs), 1578, 1451, 1354, 1325, 1289, 1272, 1230, 1206, 1194, 1148, 1111, 1014, 917, 895, 866, 839, 781, 745, 672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (sym m, 2H), 1.23 (sym m, 4H), 1.34 (sym m, 1H), 1.58 (sym d, 1H), 1.65 (sym m, 4H), 1.87 (sym m, 2H), 3.27 (s, 2H), 3.44 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 24.98, 25.08, 25.35, 26.27, 40.53, 47.79, 147.28, 150.86, 181.73; GC–MS M^+ 254. 1,4-Ethano-5,8-methano-1,4,5,6,7,8-hexahydro-9,10-anthraquinone[13] (**12**): mp 148 °C; IR (KBr) 2973, 2956, 1645 (vs), 1576, 1333, 1321, 1291, 1270, 1228, 1186, 1156, 1142, 1114, 1093, 882, 832, 781, 745, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (sym m, 2H), 1.28 (sym m, 1H), 1.30 (sym m, 2H), 1.39 (sym m, 2H), 1.52 (sym m, 1H), 1.84 (sym m, 2H), 3.385 (s, 2H), 5.25 (s, 2H), 6.33 (t, 2H); ^{13}C NMR ($CDCl_3$) δ 24.63, 24.99, 33.62, 40.46, 47.85, 133.93, 147.83, 150.70, 181.21; GC–MS M^+ 252. 1,2,3,4,5,6,7,8-Octahydro-9,10-anthraquinone[13] (**13**): mp 183–184 °C; IR (KBr) 2944, 2889, 2870, 1640 (vs), 1619, 1465, 1423, 1358, 1295, 1188, 973, 808, 707, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (sym m, 8H), 2.32 (sym m, 8H); ^{13}C NMR ($CDCl_3$) δ 21.08, 22.37, 141.68, 187.38; GC–MS M^+ 216. 2,6-Di-*tert*-butyl-1,4-benzoquinone (**14**): mp 65–67 °C (Aldrich). Tetra-*tert*-butyldiphenoquinone (**15**): ^1H NMR ($CDCl_3$) δ 1.31 (s, 36 H), 7.66 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ: 29.54, 35.97, 125.97, 136.09, 150.36, 186.38.

Reduction of Nitric Acid with Nitric Oxide. Anhydrous (100%) nitric acid[56] (0.1 mL) was added with the aid of a glass-tip syringe (fitted with a platinum needle) to 10 mL of dichloromethane cooled in a dry ice–acetone bath under an argon atmosphere. Gaseous nitric oxide (purified by passage through a NaOH tower and a cold trap cooled with dry ice-acetone) was then bubbled into the dichloromethane for 10 min with vigorous stirring. The nitric acid completely dissolved, and a bright blue solution of N_2O_3 was formed.[14b] A portion of the cold solution was transferred under argon pressure to a quartz cuvette fitted with a Teflon stopcock. The cuvette was sealed and cooled in a dry ice–acetone bath. The UV–vis spectrum, recorded at −78 °C, revealed a clear maximum at 684 nm for N_2O_3.[14b] In a control reaction performed simultaneously, purified gaseous NO was also bubbled under otherwise identical conditions into 10 mL of dichloromethane (without added nitric acid) cooled to −78 °C. The solution remained colorless with no absorption above 350 nm.

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