Cyclohexadienone Diazeniumdiolates from Nitric Oxide Addition to Phenolates

D. Scott Bohle* and Jerome A. Imonigie

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

Bohle@uwyo.edu

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Sterically hindered phenols react with nitric oxide under basic condititons to give either cyclohexadienone diazeniumdiolates or oximates. Phenols with 2,6-di-*tert*-butyl and 4-methyl (butylated hydroxy toluene, BHT), 4-ethyl, or 4-methoxy methylene substituents yield the corresponding 2,6-di-*tert*-butyl-2,5-cyclohexadienone-4-alkyl-4-diazeniumdiolate salts (4-methyl **1a**, 4-ethyl **3a**, 4-methoxymethylene **5a**). Phenols with 2,6-di-*tert*-butyl and 4-methylene (2,6-di-*tert*-butylphenol) substituents yield 4-methoxymethylenediazeniumdiolate (**5a**) together with 2,6-di-*tert*-butyl benzoquinone oximate (**6a**), while phenols with 2,6-di-*tert*-butyl and 4-methylenedimethylamino or hydrogen substituents yield exclusively 2,6-di-*tert*-butyl benzoquinone oximate (**6a**). Alkylation of the silver salts of **1a**, or treating the O^2-protonated diazeniumdiolate with diazomethane, both yield mixtures of O^1- and O^2-methylated isomers. All the compounds exhibit exothermic thermal decomposition except the quinuclidinium (**1e**, **3e**, **5e**) and triethylenediammonium (**1f**) salts which decompose endothermically. Three of the compounds namely "O^2-protonated" (Z)-1-[4-(2,6-di-*tert*-butyl-4-methyl-cyclohexadienonyl)]diazen-1-ium-1,2-diolinic acid (**1b**), O^2-methyl (Z)-1-[4-(2,6-di-*tert*-butyl-4-methyl-cyclohexadienonyl)]diazen-1-ium-1,2-diolate (**1c**), and "O^2-protonated" (Z)-1-[4-(2,6-di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolinic acid (**5b**) were characterized by single-crystal X-ray diffraction studies. The diazeniumdiolate framework in all the structures is coplanar with considerable π-bonding delocalized over the O−N−N−O framework.

Introduction

Phenols are an important class of antioxidants and find roles in biological systems and food additives.[1] The mechanism of the antioxidant activity of phenols is widely known to involve their ability to act as free radicals scavengers by H-atom abstraction or electron-transfer process leading to the formation of phenoxy radicals.[2,3] The reactions of phenolic antioxidants with electrophiles or radicals have been known for many years to yield the corresponding cyclohexadienone derivatives.[4−6] Although the reactions of HNO_3 [4] or nitric oxide [5,6] with phenolic antioxidants has been reported to yield the corresponding *p*-nitro- and nitrosocyclohexadienone derivatives, respectively, the reactions of phenolic antioxidants with nitric oxide in alkaline conditions have not been reported. Although the autoxidation of phenols is generally believed to involve free radical mechanisms, in alkaline conditions, a nonradical mechanism involving the addition of electrophilic agent to a phenolate anion has been reported.[4,7] The mechanism for the reaction of nitric oxide with substituted phenols in neutral conditions is believed to involve the oxidation of the phenol to a phenoxy radical which rapidly couples with nitric oxide radical to yield the para-substituted cyclohexadienone nitroso derivative.[4,6] The presence of bulky substituents, such as *tert*-butyl groups ortho to the oxygen-bearing carbon, stabilize this phenol−cyclohexadienone rearrangement.[4] Studies have shown that the formation of a stable para-substituted cyclohexadienone derivatives depends strongly on the nature of the para substituents.[4] If the bond between the para substituents and the aromatic ring is relatively weak, elimination of the para substituents is observed to give quinoid-like species rather than leading to the formation of para-substituted cyclohexadienone derivatives.[4]

The reaction of nitric oxide (NO) with ketones in basic conditions[8] (eq 1) and secondary amines[9−13] (eq 2) to produce the corresponding diazeniumdiolates are established high yield reactions. The dialkylamine derivatives from eq 2 are of considerable current pharmacological interest due to their spontaneous liberation of nitric oxide under physiological conditions.[13,14] Other naturally occurring *N*-hydroxydiazeniumdiolates, namely alano-

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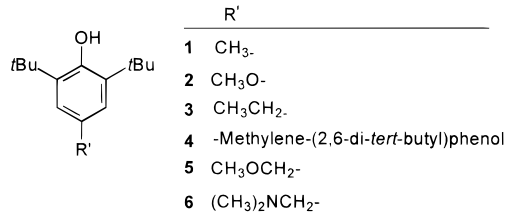
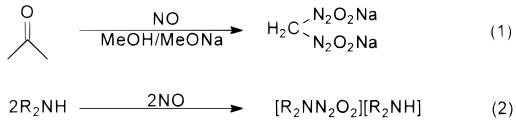
Chart 1



sine[15−17] and dopastin,[15] have also been reported to exhibit anti-bacteria and anti-cancer activities.



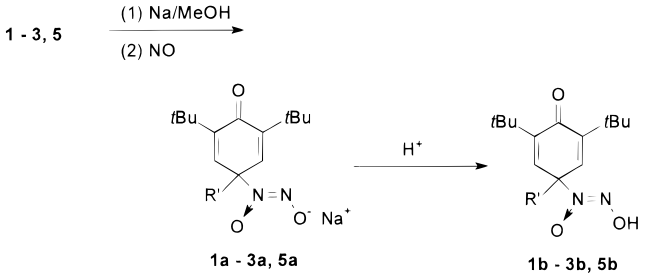
Recently, we reported the alkylation reactions of silver hyponitrite with *tert*-butyl bromide and *tert*-amyl bromide which yield both O/O- and O/N-dialkylated products.[18] As part of our research efforts toward the synthesis of compounds containing oxy-anions of nitrogen or nitroxy groups, we were interested in investigating the reaction of nitric oxide with phenolic antioxidants in basic conditions. We observed that the reaction of nitric oxide with 2,6-di-*tert*-butyl-4-methyl-phenol (butylated hydroxy toluene, BHT) (**1**) in basic conditions yielded the corresponding diazeniumdiolate derivative, whereas similar reactions in nonbasic conditions yielded no diazeniumdiolate. In view of these results, and given the current biological interest in this class of compounds, we decided to investigate the reaction of nitric oxide with the phenols in Chart 1: 2,6-di-*tert*-butyl-4-methyl-phenol (BHT) (**1**), 2,6-di-*tert*-butyl-4-methoxy-phenol (**2**), 2,6-di-*tert*-butyl-4-ethyl-phenol (**3**), 4′,4-methylene-bis(2,6-di-*tert*-butylphenol) (**4**), 2,6-di-*tert*-butyl-4-methoxymethylene-phenol (**5**), and 2,6-di-*tert*-butyl-4-dimethylaminomethylene-phenol (**6**) under basic conditions.

In this paper, we report (i) the synthesis and characterization of substituted cyclohexadienone derivatives of diazeniumdiolate, (ii) synthesis and characterization of a substituted cyclohexadienone derivative of O^2-protonated diazeniumdiolate, (iii) synthesis, separation, and characterization of substituted cyclohexadienone derivatives of O^2- and O^1-methylated isomers, (iv) the structures of three of these derivatives, and (v) the thermal decomposition studies (DSC) and UV−visible spectrophotometric studies of these compounds.

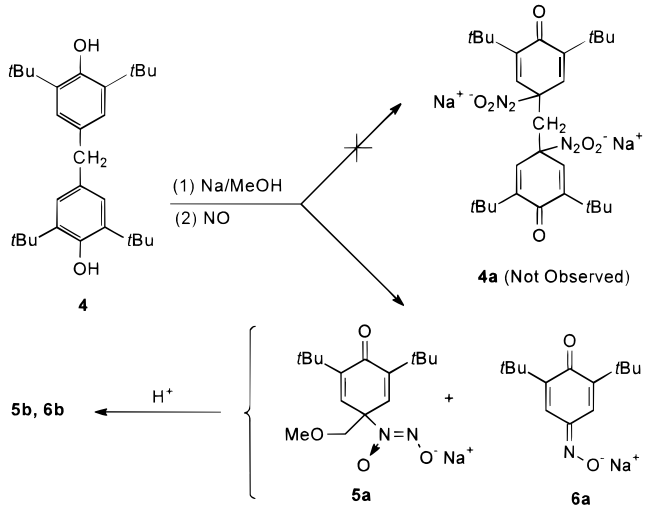
Results and Discussion

The reaction of nitric oxide with several substituted phenols in base yields the corresponding diazeniumdiolates, Scheme 1. In base, these reactions occur readily in methanol under 30−40 psi nitric oxide at room temperature and are often complete within several hours. Similar base-promoted reactions of nitric oxide with

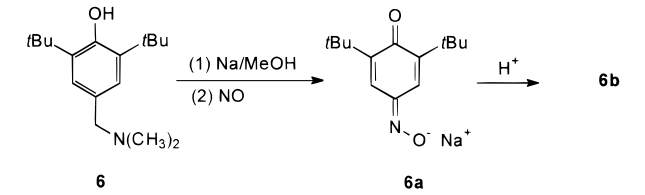
Scheme 1



Scheme 2



Scheme 3



sulfite,[19,20] ketones,[8] and secondary amines[9−13] to form diazeniumdiolates require longer periods of time. As shown in Scheme 2, the reaction of nitric oxide with **4** does not yield the expected bis(diazeniumdiolate) **4a**, but instead a mixture of **5a** and **6a** is observed. Similarly, the reaction of nitric oxide with **6** in base exclusively forms the oximate **6a** (Scheme 3). The formation of unsubstituted benzoquinone oxime has also been reported to result from the addition of nitric oxide to phenol, and in the reaction of one equivalent of hydroxylamine with benzoquinone.[21]

The new cyclohexadieneone diazeniumdiolates **1a** and **2a** precipitate from the methoxide reaction solutions and are thus readily isolated in high yield by direct filtration. Owing to their higher methanol solubility, the products **3a** and **5a** are isolated by converting them to their water-insoluble free acids. In general, as shown in Table 1, the reactions of a given substituted phenolate with nitric oxide produces a diazeniumdiolate only when the ortho substituents were *tert*-butyl groups and the para substituents were methyl, methoxy, and ethyl groups. When

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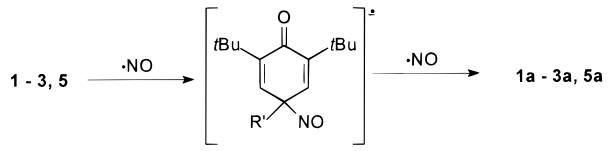
Table 1. Formation of Diazenium Diolates and Oximes as a Function of Para Substituents (R′)

para substituents (R′)	ortho substituents (R)	diazenium diolate (yield, %)	oximate (yield, %)
CH_3	$(CH_3)_3C$	yes (80)	no
CH_3O	$(CH_3)_3C$	yes (78)	no
CH_3CH_2-	$(CH_3)_3C$	yes (88)	no
methylene(2,6-di-*tert*-butyl)phenol	$(CH_3)_3C$	yes (60)	yes (56)
$(CH_3)_2NCH_2$	$(CH_3)_3C$	no	yes (68)
H	$(CH_3)_3C$	no	yes (82)
$(CH_3)_2C$	$(CH_3)_3C$	no	no
CH_3	CH_3	no	no

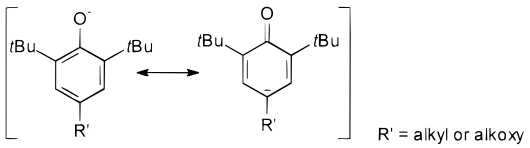
Scheme 4



B

the para substituent is a 2,6-di-*tert*-butyl-4-methylenephenolic group, a 1:1 mixture of diazeniumdiolate (**5a**) and oximate (**6a)** is produced. On the other hand, when the para substituent is methylenedimethylamino or a proton, the corresponding oximate (**6a**) forms exclusively. However, if the substituents at both ortho and para positions are either *tert*-butyl or methyl groups, no diazeniumdiolate or oximate is isolated and the reaction is a complex intractable mixture.

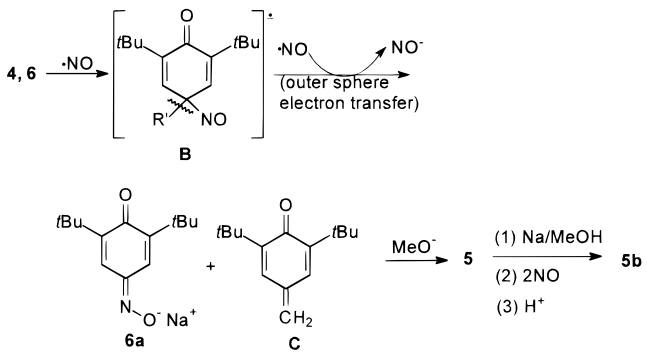
Resonance delocalization of the negative charge in phenolates results in considerable negative charge on the para carbon:



A

In addition, the bulky *o*-*tert*-butyl substituents reduce the reactivity at these carbons and reinforce the buildup of charge density at the para-carbon.[22,23] Therefore, even relatively weak electrophiles such as nitric oxide will readily add to the para carbon in phenolates. Thus, the mechanism for the addition of nitric oxide to **1**−**3** and **5** to produce diazeniumdiolates **1a**−**a** and **5a** can be understood in terms of an initial electrophilic addition of nitric oxide to a phenolate anion at the para position to form a nitroso cyclohexadienone radical anion intermediate, **B**, Scheme 4. The intermediate **B** undergoes an additional nitric oxide coupling to form the observed diazeniumdiolates as shown in Scheme 4. This mechanism is directly analogous to that proposed by Drago for the reaction of nitric oxide with secondary amine to form $R_2NN_2O_2^-$[9−13] and for the reaction of bisulfite with nitric oxide in basic medium.[19,20] The reaction of nitric oxide with bisulfite, as proposed by Drago, is an excellent example of nitric oxide's electrophilicity.[9] In this mechanism, the radical anion intermediate has a π^*-orbital

Scheme 5



SOMO delocalized over the NO, and this stereospecifically couples with another nitric oxide to form a new nitrogen−nitrogen double bond with a *Z* configuration in the $[O_3SN_2O_2]^{2-}$ product.[24] This mechanism probably operates in the reactions shown in Scheme 1, and we note that we have never seen, nor are we aware of any experimental evidence for, the products of these reactions having an *E* geometry at the resulting N=N. Other workers note that the presence of a *tert*-butyl group in ortho position tends to stabilize the formation of cyclohexadienone derivatives.[4] Similar stabilization effects are also observed for the formation of cyclohexadienone diazeniumdiolate products in this study. The lack of formation of diazeniumdiolate from phenolate containing a *tert*-butyl moiety at the para position may be explained in terms of the steric effects imposed by the bulky *tert*-butyl group at the para position. Conversely, the lack of formation of diazeniumdiolate when the substituents at the ortho positions are methyl groups is also consistent with the fact that only bulky *tert*-butyl groups stabilize the formation of the cyclohexadienone structure.

The mechanism for the reaction of nitric oxide with **4** and **6** to produce oximate **6a** probably also involves an initial electrophilic addition of nitric oxide to the para carbon of the phenolate to form a nitroso cyclohexadienone radical anion intermediate, **B**. Possibly, the relatively bulky para substitutuents (2,6-di-*tert*-butyl-4-methylene-phenol **4** and methylenedimethylamino **6**), prevent the coupling of another nitric oxide to the radical anion intermediate, which may then undergo subsequent outer-sphere electron-transfer reaction with another nitric oxide to form nitric oxide anion (NO^-), followed by an elimination of the para substituent to form an oximate (**6a**) as shown in Scheme 5. Similar elimination reactions of phenols with para-substituents such as −H, $-CH_2OH$, −CHO, −COOH, and other substituents with an α-carbon atom linked to nitrogen and oxygen functional groups following an electrophilic addition are known.[4] This elimination was ascribed to the relatively weak bond between the substituents and the aromatic ring. However, the elimination of substituents such as $-CH_2OCH_3$ and $-OCH_3$ was *not* observed in this study. One factor contributing to the heterolytic elimination of 2,6-di-*tert*-butyl-4-methylenephenol and methylenedimethylamino substituents may simply be sterics, rather than to carbon−carbon bond homolysis from **B** in the intermediate. In the case of the reaction of nitric oxide with **4**, this mechanism gives rise to the *p*-quinone methide intermediate (**C**). The electrophilicity of methylene in *p*-quinone

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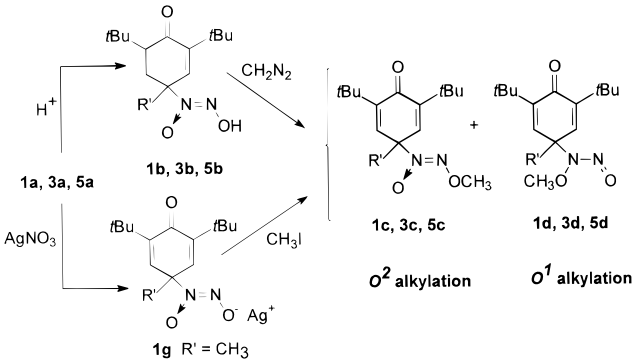
Scheme 6



methides is well established,[25−27] and under our conditions it would be expected to rapidly add methoxide to give 2,6-di-*tert*-butylmethoxymethylene phenolate (**5**) in Scheme 5. The resulting 2,6-di-*tert*-butylmethoxymethylene phenolate (**5**) subsequently reacts with two nitric oxides by the same mechanism in Scheme 1, to form the observed diazeniumdiolate product **5a**, Scheme 5. The addition of acid to **5a** leads to the formation of the protonated product **5b**. In contrast with the sodium salts **1a** and **2a**, which precipitate as colorless solids from methanol, the sodium salts **3a** and **5a** are very soluble in methanol.

O^2-Protonated diazeniumdiolates (**1b**, **3b**, **5b)** are readily prepared by the addition of 0.1 M HCl solution (Scheme 6). However, the diazeniumdiolate sodium salt **2a** decomposes to the corresponding benzoquinone upon addition of acid or any other Lewis acid such as transition metal complexes.

Unlike the well-known cyclohexadienone−phenol rearrangement, which involve the acid-catalyzed conversion of a cyclohexadienone to the corresponding phenol,[28] the addition of equimolar or excess amounts of acid to the diazeniumdiolate sodium salts **1a**, **3a**, and **5a**, yields exclusively the corresponding O^2-protonated diazeniumdiolates; no formation of a substituted phenol is observed. Although a few diazeniumdiolinic acids are relatively stable,[29] many readily decompose upon protonation or in the presence of excess acid.[30] The present series of salts are quite stable in acidic conditions, and the protonated compounds (**1b**, **3b**, and **5b**) are insoluble in water but soluble in most apolar and polar solvents.

The alkylation of the **1g** with methyl iodide or O^2-protonated diazeniumdiolate (**1b**, **3b**, **5b**) with diazomethane yielded two geometric isomers (**1c** and **1d**, **3c** and **3d**, **5c** and **5d**) as shown in Scheme 6. The basis for these assigned structures is it follows Hickmann et al.'s suggestion[30] and it best fits the IR and NMR spectroscopic data described below. However until one of the members of the O^2-alkylated family of compounds **d** is structurally characterized with X-ray diffraction, these assignments await further confirmation. Diazomethane is a particularly useful alkylation agent for stable *N*-

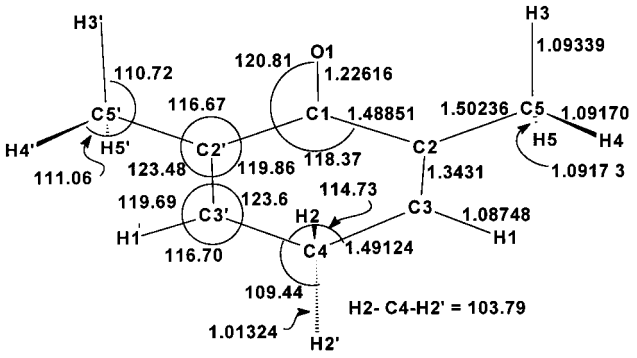
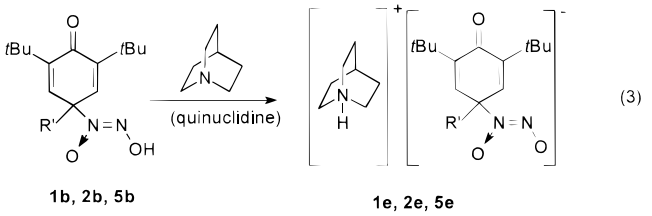


Figure 1. Calculated ab initio ground-state geometry for 2,6-dimethyldienone with a C_{2v} geometry (B3LYP/6-311++G**). Bond lengths are given in Å and angles in deg.

hydroxydiazeniumdiolates. The ratio of the isomers depends on the alkylating agent as well as the substrate. It is noteworthy that the ratio of O^2 (**1c**) to O^1 (**1d**)-isomeric products obtained from diazomethane alkylation was found to be lower (5:1) than with methyl iodide alkylation (15:1). However, under both conditions, O^2-methylated isomer is always the predominant isomer. The isomeric products were easily separated and isolated by preparative chromatography or preparative TLC. The formation of both the nitroso (from O^1-alkylation) and alkyl diazeniumdiolate (from O^2-alkylation) in 1:5 ratio suggests that following proton transfer, which gives the highly electrophilic $CH_3N_2^+$, either oxygen is readily alkylated.

The reaction of quinuclidine with the protonated derivatives yielded the corresponding quinuclidinium salts (eq 3), which are insoluble in ether but soluble in most polar solvents such as H_2O, CH_2Cl_2, CH_3CN, and MeOH.



(3)

Spectroscopic Results. In addition to the strong characteristic bands due to the diazeniumdiolates in these products, the IR spectra of the cyclohexadienone moiety also contains a number of strong bands, typically two, in the carbonyl stretching region. To understand in greater detail the origin of these bands, we have performed ab initio density functional calculations on a representative framework model for this system, 2,6-dimethylcyclohexadienone. The calculated (B3LYP/6-311++G**) optimized ground-state structure, with a C_{2v} geometry shown in Figure 1, clearly contains the alternating ring carbon−carbon bond lengths predicted by valence bond theory. The mid-energy vibrational modes for the cyclohexadienone ring are shown in Figure 2 and illustrate how the coupling of the carbonyl stretch to the ring breathing modes results in an asymmetric and symmetric combination of these modes, with the former being particularly intense in the infrared spectrum. The original parent cyclohexadienone, without the methyl groups, has also been calculated, but in this case the 2,6-protons couple strongly into these modes, and the normal

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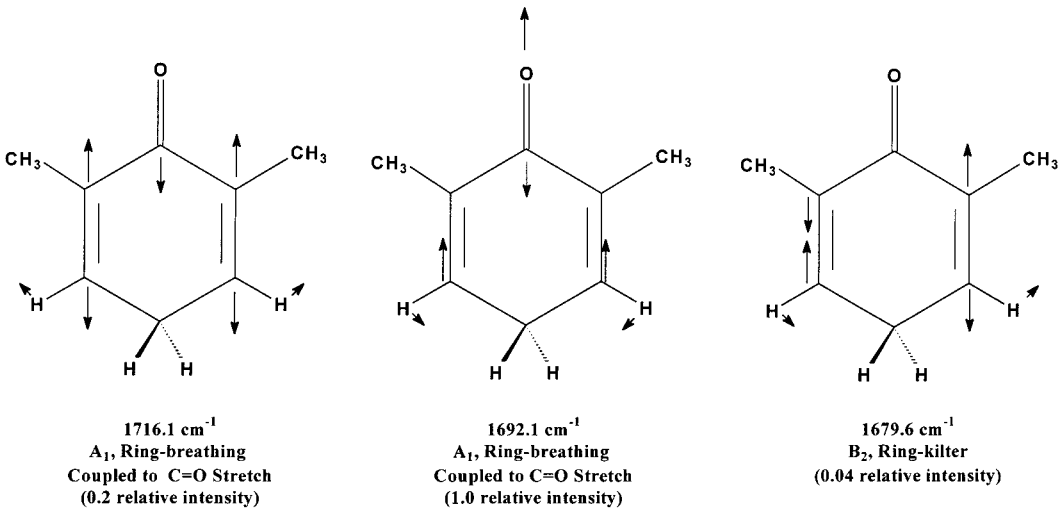

Figure 2. Calculated coupling of the carbonyl and ring breathing modes for 2,6-dimethyldienone with the geometry shown in Figure 1. Energies and modes predicted by ab initio density function theory, B3LYP/6-311++G**.

coordinates and energies for these transitions match poorly with the experimental data. In general, the anionic diazeniumdiolate substituted cyclohexadienone derivatives all have two strong bands between 1670 and 1640 cm^{-1}.

The sodium (**1a**, **2a**, **3a**, **5a**), quinuclidium (**1e**, **3e**, **5e**), and DABCO (**1f**) salts exhibit a UV−vis absorption between 246 and 250 nm which is typical for $\pi-\pi^*$ transition for diazeniumdiolate. The UV−vis absorption for the O^2-protonated derivatives (**1b**, **3b**, and **5b**) exhibit characteristic $\pi-\pi^*$absorptions at 234 nm. However, the O^2- (**1c, 3c, 5c**) and O^1- (**1d**) methylated isomers exhibit $\pi-\pi^*$ transition bands at 236 and 238 nm, respectively. As expected for nitroso compounds, which typically have weak n−π^* transitions near 372 nm,[31,32] the UV spectra of compound **1d** uniquely has this band. But a careful examination of all the UV−vis spectra of cyclohexadienone diazeniumdiolates at higher concentrations reveals a similar weak n−π^* transition at 372 nm in methanol ascribed to this group. Therefore, the n−π^* transition at 372 nm observed for the nitroso derivative is probably due to an overlap of these bands which preclude definitive assignment of the nitroso n−π^* transitions. As expected for a typical n−π^* transition, a bathochromic effect or red shift with decreasing solvent polarity was observed (cyclohexane 382 nm).

The ^1H and ^{13}C NMR of all the sodium salt, O^2-protonated and O^2-methylated compounds are similar with negligible differences in their chemical shifts. There are however significant chemical shift differences for the O^1- and O^2-methylated isomers. Specifically, in compound **1d**, the cyclohexadienone protons (6.68 ppm) and the methoxy protons (3.83 ppm) are shifted more upfield compared to **1c**, 6.81 and 4.05 ppm, respectively. On the other hand, the methyl protons (1.83 ppm) of **1d** are more downfield compared to the **1c** isomer (1.77 ppm). Similarly, the ^{13}C NMR spectra for **1c** and **1d** isomers are also significantly different. In particular, the chemical shift of C1-atom of the **1c** isomer is more downfield (73 ppm), while the C1-atom of **1d** isomer is more upfield (66 ppm). However, the chemical shift for the methoxy carbon of the **1d** isomer is also more downfield (65 ppm) compared to the **1c** isomer (62 ppm). Similar chemical shift differences have been reported for the two isomers obtained from the alkylation of the silver salt of *N*-nitroso(*cis*-4-methylcyclohexyl)hydroxylamine with methyl iodide.[29]

Table 2. Differential Scanning Calorimetric Data

compd	T_{onset} (°C)	T_{max}(°C)	ΔH (cal/g)	ΔH (kcal/mol)
1a	195	200	−55.3	−6.72
1b	83.4	88.3	+17.2	+4.82
	95.4	109	−63.7	−17.8
1c	84.6	98.4	−211	−62.1
1d	82.9	109	−180	−52.9
1e	125	128	+31.4	+12.3
1f	119	121	+16.0	+6.30
2a	198	206	−85.1	−27.1
3b	89.6	91.6	+23.3	+6.87
	198	206	−85.1	−25.1
3c	68.4	84.3	−172	−53.0
3e	106	113	+42.3	+13.0
5b	116	119	+19.0	+5.59
	124	130	−13.4	−3.94
5c	102	104	−182	−59.2
5e	103	113	+67.0	+28.2
6b	221	228	+44.86	+10.57

Differential scanning calorimetry has been used to characterize the thermal stability of all new compounds, Table 2. Although all of these species are stable up to ∼100 °C, further heating leads to irreversible decomposition. Whereas the sodium and silver salts decompose exothermally, the quinuclidinium (**1e**, **3e**, **5e**) and triethylenediammonium (**1f**) decompose endothermally. Also, whereas the O^1- and O^2-methylated isomers exhibit a single exothermic process, the O^2-protonated derivatives (**1b**, **3b**, **5b**) exhibit both endothermic and exothermic process. However, in contrast with the generally greater reactivity of nitroso compounds the O^1-methylated nitroso isomer (**1d**) was found to be more thermally stable (T_d = 109 °C) than the O^2-methylated isomer (**1c**) (T_d = ∼ 98 °C).

Structural Data. Compounds **1b**, **1c**, and **5b** have been characterized by single-crystal X-ray crystallography. ORTEP views of these structures are given in Figure

(31) Challis, B. C.; Challis, J. A. *In the Chemistry of Functional Groups. Supplement F. The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1982; p 1176.

(32) Rao, C. N. R.; Bhaskar, K. R. *The Chemistry of the Nitro- and Nitroso Groups;* Feuer, H., Ed.; John Wiley & Sons: New York, 1969; Part 1, pp 152−155.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 1c, 1c, and 5b

compd	N=N (Å)		N−O (Å)		N−N−O (deg)		other bond lengths (Å)	
1b	N(1)−N(2)	1.270 (2)	N(1)−O(2)	1.367 (2)	N(1)−N(2)-O(3)	122.5 (2)	C(1)−O(1)	1.220 (2)
			N(2)−O(3)	1.273 (2)	N(2)−N(1)-O(2)	108.9 (2)	C(2)−C(3)	1.332 (3)
							C(5)−C(6)	1.328 (3)
1c	N(1)−N(2)	1.272 (2)	N(1)−O(2)	1.379 (3)	N(1)−N(2)-O(3)	126.0 (2)	C(1)−O(1)	1.212 (3)
			N(2)−O(3)	1.260 (2)	N(2)−N(1)-O(2)	109.1 (2)	C(2)−C(3)	1.333 (3)
							C(5)−C(6)	1.333 (3)
5b	N(1)−N(2)	1.279 (3)	N(1)−O(2)	1.368 (3)	N(1)−N(2)-O(3)	123.8 (2)	C(1)−O(1)	1.221 (3)
			N(2)−O(3)	1.266 (3)	N(2)−N(1)-O(2)	110.1 (2)	C(2)−C(3)	1.335 (3)
							C(5)−C(6)	1.338 (3)

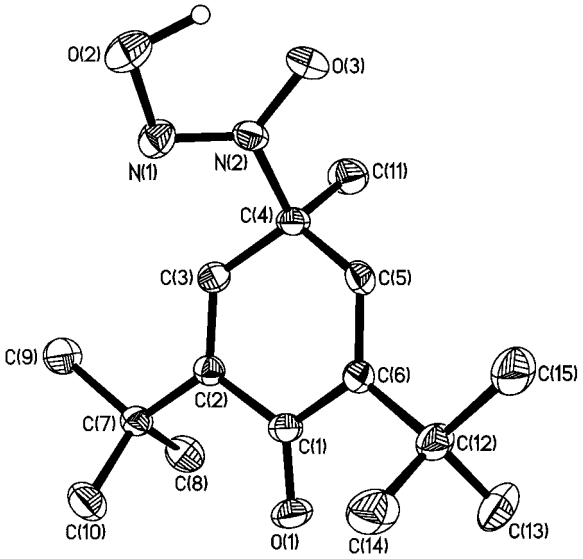

Figure 3. ORTEP view of one of the three independent molecules of **1b** in the asymmetric unit. All non-hydrogen atoms shown.

3 and Figures S1 and S2 (Supporting Information). Selected bond distances and angles are listed in Table 3.

Crystals of compound **1b** uniquely contains three structurally similar molecules (only one molecule is shown in Figure 3) in the crystallographic asymmetric unit. In the final refinement of **1b**, all related atoms in the three independent molecules refine without correlation to one another and overall there are no correlation coefficients greater than 0.5 between two chemically related atoms. The diazeniumdiolate fragments in structures **1b**, **1c**, and **5b** are coplanar with similar bonding features. The diazeniumdiolate fragment in these structures adopts a *Z* geometry with metrical parameters similar to those reported for related compounds.[29] In general, the average N1−N2 bond distance (1.274 Å) is significantly longer than a typical double bond distance, whereas the average N1−O2 (1.371 Å) and N2−O3 (1.266 Å) bond distances are considerably shorter than a typical single bond distance. These observations are consistent with π-bond delocalization over the O1−N1−N2−O2 framework. Similar bonding features have been reported for related compounds.[29] Also, the average C2−C3 (1.333-(3) Å) and C5−C6 (1.333(3) Å) bond distances in the cyclohexadienone fragment in the three structures are consistent with C=C double distances, and there is clear single-double bond alteration in the ring. Moreover, the average C1−O1 (1.221(2) Å) bond distances in all three compounds are also consistent with a typical bond distance of a ketonic group, and all experimentally determined bond distances in the cyclohexadienone ring compare with those calculated with density functional theory, Figure 1.

Conclusion

The reaction of nitric oxide with many sterically congested phenols in basic conditions yields cyclohexadienone diazeniumdiolates. The presence of a bulky *tert*-butyl group in the ortho positions and alkyl group in the para-position stabilize the formation of cyclohexadienone diazeniumdiolate. The alkylation of *N*-hydroxydiazeniumdiolinic acid with diazomethane yields both O^1- and O^2-methylated isomers with less selectivity toward O^2-alkylation than is seen in the products of the reaction of methyl iodide and silver diazeniumdiolate salts. The X-ray structural data indicate that the diazeniumdiolate fragment uniformly has a planar *Z* geometry, and has considerable π-bond delocalization over the O−N−N−O framework. All compounds are stable in acidic conditions, except compound **2a**, which decomposes spontaneously. Research is underway to trap the liberated NO or *cis*-hyponitrite from the Lewis acid promoted decomposition of **2a**.

Experimental Section

Materials and Methods. Nitric oxide, Scott Specialty Gases, Inc., was purified by passing through potassium hydroxide pellets to remove higher oxides of nitrogen. All chemicals and solvents were of reagent grade and were used without further purification. Diazomethane was used as a freshly generated alcohol-free ethereal solution, which was prepared by literature methods.[33] All instrumental techniques (IR, UV−vis, NMR and DSC) have been described previously.[18,34]

Synthesis of Sodium (Z)-1-[4-(2,6-Di-*tert*-butyl-4-methylcyclohexadienonyl)]-diazen-1-ium-1,2-diolate (1a). Absolute methanol (60 mL) was treated with sodium (2.55 g, 0.11 mol) under nitrogen with stirring until the reaction was finished and the temperature returned to ambient conditions. To this solution was added 2,6-di-*tert*-butyl-4-methylphenol (**1**) (5.3 g, 0.024 mol), the solution was filtered, and the clear pale yellow solution was transferred to a glass pressure reaction bottle, repeatedly flushed with nitrogen, and pressurized (ca. 35 psi) with nitric oxide. The pale yellow solution immediately turned a deep yellow or yellowish brown and a white precipitate began to form within 2 h. The reaction mixture was pressurized with nitric oxide repeatedly until there was no further nitric oxide consumption as indicated by a significant drop in the pressure (24 h). Residual nitric oxide was flushed from the headspace with nitrogen, the mixture was filtered, and the solid product was thoroughly washed with ether and dried *in vacuo* at 120 °C to remove occluded methanol. ***Note:*** If the reaction is stopped immediately upon formation of the white precipitate, the product was contaminated with the unreacted sodium phenoxide. Yield: 4.62 g (80%). Anal. Calcd for $C_{15}H_{23}N_2O_3Na$: C, 59.58; N, 9.26, H, 7.67. Found: C, 59.24; N, 9.22; H, 7.65. IR (KBr, cm^{-1}): 1667 (C_6C=O, vs)$_{sym}$, 1650

(33) Technical Information Bulletin Number AL-180; Aldrich Chemical Co., Inc.: Milwaukee, WI, p 3.

(34) Arulsamy, N.; Bohle, D. S.; Imonigie, J. A.; Sagan, S. E. *Inorg. Chem.* **1999**, *38*, 2716−2725.

($C_6C{=}O$, vs)$_{asym}$. UV−vis (H_2O, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 250 (15 1 40). ^1H NMR (CD_3OD, 100 MHz) δ: 1.23 (s, 18 H), 1.67 (s, 3H), 7.01 (s, 2H). ^{13}C NMR (CD_3OD, 400 MHz) δ: 187.4, 146.6, 141.6, 68.6, 35.9, 29.9, 26.2.

Synthesis of "O^2-Protonated" (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolinic Acid (1b). To a methanol solution of **1a** (1.68 g, 0.0056 mol) was added dropwise 0.1 M HCl solution with stirring until no further precipitate of **1b** formed. The precipitate was filtered, washed with water, and dried. The crude product was dissolved in hexane (50 mL), and the solution was filtered to remove any insoluble solid. On evaporation of the filtrate colorless crystals were obtained. Yield: 1.25 g (80%). Anal. Calcd for $C_{15}H_{24}N_2O_3$: C, 64.03; H, 8.96, N, 9.96. Found: C, 63.80; H, 8.53; N, 9.87. IR (KBr, cm^{-1}): 1668 ($C_6C{=}O$, vs)$_{sym}$, 1648 ($C_6C{=}O$,vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 234 (14 471). ^1H NMR (CD_3OD, 400 MHz) δ: 1.25 (s, 18H), 1.80 (s, 3H), 6.78 (s, 2H), 11.68 (s, 1H). ^{13}C NMR (CD_3OD, 100 MHz) δ: 185.1, 148.9, 135.3, 71.9, 35.4, 29.4, 26.1.

Synthesis of *O*^{2}-Methyl (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (1c). Method A. To a solution of **1b** (0.43 g, 0.0015 mol) in ether (25 mL) was slowly added an ethereal solution of diazomethane that was prepared according to literature procedures,[33] with stirring at 0−5 °C. There was immediate effervescence. The diazomethane addition was continued until the yellow color of diazomethane persisted. The solution was then evaporated with a stream of nitrogen gas in an efficient hood to yield a ∼5:1 mixture of *O*^{2}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (**1c**) and *O*^{1}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methyl-cyclohexadienonyl)]-diazen-1-ium-1,2-diolate (**1d**) isomers as a yellow crystalline product. Yield: 0.41 g, (91%). The two isomers were separated by preparative silica gel chromatography or by preparative silica gel TLC plates using CH_2Cl_2 as the eluent. The first fraction contained the *O*^{1}-methyl isomer (**1c**) (0.07 g) and the second fraction contained the *O*^{2}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methyl-cyclohexadienonyl)]diazen-1-ium-1,2-diolate (**1d**) (0.34 g).

O^2-Methyl (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methyl-cyclohexadienonyl)]diazen-1-ium-1,2-diolate (**1c**). Anal. Calcd for $C_{16}H_{26}N_2O_3$: C, 65.28; H, 8.90; N, 9.51. Found: C, 65.22; H, 8.96; N, 9.42. IR (KBr, cm^{-1}): 1668 ($C_6C{=}O$, vs)$_{sym}$, 1648 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 236 (15 337). ^1H NMR (CD_3OD, 400 MHz) δ: 1.25 (s, 18H), 177 (s, 3H), 4.05 (s, 3H), 6.81 (s, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 185.4, 147.9, 136.5, 73.3, 61.6, 35.3, 29.5, 26.2.

O^1-Methyl (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methyl-cyclohexadienonyl)]diazen-1-ium-1,2-diolate (**1d**). Anal. Calcd for $C_{16}H_{26}N_2O_3$: C, 65.28; H, 8.90, N, 9.51. Found: C, 65.02; H, 8.88; N, 9.29. IR (KBr, cm^{-1}): 1667 ($C_6C{=}O$, vs)$_{sym}$, 1645 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 238 (11 492). ^1H NMR (CD_3OD, 400 MHz) δ: 1.25 (s, 18 H), 183 (s, 3H), 3.83 (s, 3H), 6.68 (s, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 185.5, 148.4, 137.7, 65.8, 64.9, 35.2, 29.8, 25.7.

Synthesis of Quinuclidinium (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (1e). To a solution of **1b** (0.24 g, 0.00086 mol) in ether (30 mL) was added dropwise a solution of quinuclidine (0.1 g, 0.0009 mol) in ether (25 mL) with stirring at 0−5 °C. The precipitated white solid (**1e**) was filtered and dried in vacuo over P_2O_5. Yield: 0.314 g (96%). Anal. Calcd for $C_{22}H_{37}N_3O_3$: C, 67.48; H, 9.52, N, 10.73. Found: C, 67.24; H, 9.47; N, 10.73. IR (KBr, cm^{-1}): 1663 ($C_6C{=}O$, vs)$_{sym}$, 1640 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 246 (12,914). ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.24 (s, 18 H), 1.71 (s, 3H), 1.75−1.80 (m, 6H), 2.05 (sept, 1H, J = 3.15 Hz), 3.17 (t, 6H, J = 8.10 Hz), 6.95 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 186.4, 145.5, 139.6, 67.7, 46.8, 35.0, 29.5, 25.2, 24.1, 20.0

Synthesis of Triethylenediammonium (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (1f). This compound was prepared from the reaction of **1b** (0.50 g, 0.0018 mol) with triethylenediamine (DABCO) (0.22 g, 0.002 mol) by the procedure described above for **1e.** Yield: 0.64 g (91%). Anal. Calcd for $C_{21}H_{36}N_4O_3$: C, 64.25; H, 9.24; N, 14.27. Found: C, 64.11; H, 9.23; N, 13.85. IR (KBr, cm^{-1}): 1666 ($C_6C{=}O$, vs)$_{sym}$, 1641 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 240 (11,128). ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.25 (s, 18 H), 1.77 (s, 3H), 2.89 (s, 6H), 6.84 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 186.4, 147.9, 136.7, 46.9, 35.3, 29.5, 26.2.

Synthesis of *O*^{2}-Methyl (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (1c). Method B. Silver (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate **(1g)** (1.36 g, 0.035 mol), freshly prepared from the reaction of aqueous solutions of silver nitrate and **1a**, and well-dried, was added in small amounts to a solution of methyl iodide (3 mL, 0.048 mol) in ether (50 mL) at 0−5 °C with stirring. The solution was stirred for 2 h and filtered to remove silver iodide. The filtrate was evaporated in the hood by bubbling nitrogen through the headspace to yield *O*^{1}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (**1c**) and *O*^{2}-methyl (Z)-1-[4-(2,6-di-*tert*-butyl-4-methylcyclohexadienonyl)]-diazen-1-ium-1,2-diolate (**1d**) isomeric mixture (15:1) as a yellow solid. Yield: 0.81 g (79%). The isomers were separated as described in method **A**.

Synthesis of Sodium (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methoxycyclohexadienonyl)]diazen-1-ium-1,2-diolate (2a). This compound was synthesized from the reaction of 2,6-di-*tert*-butyl-4-methoxyphenol **2** (3.77 g, 0.016 mol) with nitric oxide by the procedure described for the synthesis of **1a**. Yield: 3.98 (78%). Anal. Calcd for $C_{15}H_{23}N_2O_4Na$: C, 56.60; H, 7.28; N, 8.80. Found: C, 56.20; H, 7.14; N, 8.77. IR (KBr, cm^{-1}): 1670 ($C_6C{=}O$, vs)$_{sym}$, 1649 ($C_6C{=}O$, s)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 254 (13 042). ^1H NMR (CD_3OD, 400 MHz) δ: 1.22 (s, 18 H), 3.31 (s, 3H), 6.97 (s, 2H). ^{13}C NMR (CD_3OD, 100 MHz) δ: 187.4, 148.9, 135.5, 90.8 52.0, 36.2, 29.9.

Synthesis of "O^2-Protonated" (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-ethylcyclohexadienonyl)]diazen-1-ium-1,2-diolinic Acid (3b). The reaction of 2,6-di-*tert*-butyl-4-ethylphenol (**3**) (5.15 g, 0.022 mol) with nitric oxide in the presence of sodium methoxide carried out as described for **1a** did not yield any precipitate of sodium (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methoxycyclohexadienonyl)]diazen-1-ium-1,2-diolate (**3a**). The O^2-protonated product **3b** was readily precipitated from the resultant reddish solution on treatment with 0.1 M hydrochloric acid until no more precipitate was formed as described in the synthesis of **1b**. Yield: 5.70 g (88%). Anal. Calcd for $C_{16}H_{26}N_2O_3$: C, 65.28; H, 8.90; N, 9.51. Found: C, 65.23; H, 9.02; N, 9.56. IR (KBr, cm^{-1}): 1667 ($C_6C{=}O$, vs)$_{sym}$, 1645 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 234 (13,-440). ^1H NMR (CD_3OD, 400 MHz) δ: 0.82 (t, 3H, J = 7.46 Hz), 1.22 (s, 18 H), 2.21 (q, 2H, J = 7.46 Hz), 3.31 (s, 3H), 6.97 (s, 2H), 11.8 (s, 1H); ^{13}C NMR (MeOD) δ: 185.4, 150.2, 133.9, 75.6, 35.6, 32.1, 29.5, 8.12.

Synthesis of *O*^{2}-Methyl (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-ethylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (3c). This compound is prepared as described for **1c (**method **A)** by treating **3b (**0.43 g, 0.0015 mol) with diazomethane to yield a mixture of *O*^{2}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-ethylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (**3c**) and *O*^{1}-methyl (Z)-1-[4-(2,6-di-*tert*-butyl-4-ethylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (**3d**) isomeric mixture (10:1) as a yellow solid. Yield: 0.40 g (89%). The product mixture is unstable in air and found to turn to dark liquid on standing for several hours. Therefore, no attempts were made to separate the two isomers. However, the NMR spectroscopic data of the mixture obtained within 1 h exhibited two sets of peaks corresponding to the two isomers. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 237-(13,974).

O^2-Methyl Isomer (**3c**). ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.77 (t, 3H, J = 7.42 Hz), 1.22 (s, 18H), 2.15 (q, 2H, J = 7.52 Hz), 4.02 (s, 3H), 6.75 (s, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 185.7, 149.2, 135.2, 76.0, 61.6, 35.5, 29.6, 8.14.

O^1-Methyl Isomer (**3d**). ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.81 (t, 3H, J = 7.45 Hz) 1.23 (s, 18H) 2.19 (q, 2H, J = 7.70 Hz), 3.81 (s, 3H), 6.61 (s, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 185.8, 150.0, 136.0, 76.2, 64.9, 35.4, 29.5, 8.2.

Synthesis of Quinuclidinium (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-ethylcyclohexadienonyl)]diazen-1-ium-1,2-diolate (3e). This compound was synthesized by treating **3b** (0.2 g, 0.00068 mol) with quinuclidine (0.08 g, 0.00072 mol) by the procedure described for the synthesis of **1e** as a white solid. Yield: 0.25 g (92%). Anal. Calcd for $C_{16}H_{26}N_3O_3$: C, 69.86; H, 7.39; N, 10.62. Found: C, 69.50; H, 6.10; N, 10.26. IR (KBr, cm^{-1}): 1664 ($C_6C{=}O$, vs)$_{sym}$, 1645 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 248 (9,000). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.76 (t, 3H, J = 7.49 Hz), 1.24 (s, 18H), 1.75−1.80 (m, 6H), 2.02 (sept, 1H, J = 3.20 Hz), 2.15 (q, 2H, J = 7.45 Hz), 3.20 (t, 6H, J = 8.08 Hz), 6.90 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 186.7, 147.2, 137.8, 71.7, 46.9, 35.2, 31.7, 29.7, 24.2, 20.1, 8.37.

Synthesis of "O^2-Protonated" (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolinic Acid (5b). The reaction of 4′,4-methylenebis-(2,6-di-*tert*-butylphenol) (**4**) (5.25 g, 0.013 mol) with nitric oxide carried out as described in the synthesis of **1a** did not yield any precipitate of sodium (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methoxycyclohexadienonyl)]diazen-1-ium-1,2-diolate (**5a**). The resultant reddish solution was treated with 0.1 M HCl solution until no more precipitate of **5b** was formed. The light yellow precipitate (6.35 g) formed was filtered, washed with water, and dried *in vacuo* over P_2O_5. The ^{1}H NMR spectrum of the precipitate revealed that the mixture contained "O^2-protonated" product **5b** together with 2,6-di-*tert*-butylcyclohexadienonyl-4-oxime (**6b**). From an ether solution of the mixture (1 g), the quiniclidinium salt of **5b** was readily precipitated by the dropwise addition of a solution of quinuclidine (1.04 g, 0.0094 mol) in ether at 0−5 °C. The quinuclidinium salt precipitated immediately was filtered and dried. Subsequently, the salt was dissolved in methanol and treated with 0.10 M HCl as described previously. The precipitated, "O^2-protonated" product **5b** was filtered and dried *in vacuo* over P_2O_5. Yield: 0.37 g (60%). X-ray quality crystals are obtained from the recrystallization of the product from 1:1 mixture of hexane and ether. Anal. Calcd for $C_{16}H_{26}N_2O_3$: C, 61.96; H, 8.44; N, 9.02. Found: C, 61.87; H, 8.54; N, 9.05. IR (KBr, cm^{-1}): 1669 ($C_6C{=}O$, vs)$_{sym}$, 1649 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 236 (12,008). ^{1}H NMR (CD_3OD, 400 MHz) δ: 1.26 (s, 18 H), 3.37 (s, 3H), 3.79 (s, 2H), 6.90 (s, 2H), 11.74 (s, 1H). ^{13}C NMR (CD_3OD, 100 MHz) δ: 185.3, 150.8, 131.5, 74.7, 60.2, 35.7, 30.5, 29.4.

Synthesis of *O*^{2}-Methyl (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolate (5c). The reaction of **5b** (0.40 g, 0.0013 mol) with diazomethane carried out as described in the synthesis of **1c** yielded a product mixture containing *O*^{2}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolate (**5c**) and *O*^{1}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolate (**5d**) isomers (15:1) as a yellow solid. Yield: 0.38 g (90%). Anal. Calcd for $C_{17}H_{28}N_2O_4$: C, 62.94; H, 8.70; N, 8.64. Found: C, 62.65; H, 8.68; N, 8.40. IR (KBr, cm^{-1}): 1665 ($C_6C{=}O$, vs)$_{sym}$, 1649 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 236 (15 000). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.21 (s, 18H), 3.33 (s, 3H), 3.72 (s, 2H), 4.03 (s, 3H), 6.85 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 185.5, 149.9, 132.7, 76.6, 75.9, 61.7, 60.1, 35.6, 29.5.

Note: The *O*^{1}-methyl (*Z*)-1-[4-(2,6-di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolate (**5d**) isomer was not isolated in this reaction. However, the ^{1}H NMR data obtained for the crude product mixture also exhibited the following weak peaks consistent with the assigned structure. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.21 (s, 18H), 3.36 (s, 3H), 3.64 (s, 2H), 4.18 (s, 3H), 6.78 (s, 2H).

Synthesis of Quinuclidinium (*Z*)-1-[4-(2,6-Di-*tert*-butyl-4-methoxymethylenecyclohexadienonyl)]diazen-1-ium-1,2-diolate (5e). This compound was prepared as a white solid by the procedure described for **1e** by treating **5b** (0.25 g, 0.00058 mol) with quinuclidine (0.067 g, 0.0006 mol) in ether. Yield: 0.31 g (90%). Anal. Calcd for $C_{23}H_{39}N_3O_4$: C, 65.52; H, 9.32; N, 9.97. Found: C, 65.16; H, 8.99; N, 9.65%. IR (KBr, cm^{-1}): 1665 ($C_6C{=}O$, vs)$_{sym}$, 1647 ($C_6C{=}O$, vs)$_{asym}$. UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 246 (11 688). ^{1}H NMR (CD_3OD, 400 MHz) δ: 1.24 (s, 18H), 1.80−1.85 (m, 6H), 2.09 (sept, 1H, J = 3.22 Hz), 3.20 (t, 6H, J = 8.10 Hz), 3.34 (s, 3H), 3.78 (s, 2H), 7.02 (s, 2H). ^{13}C NMR (CD_3OD, 100 MHz) δ: 186.5, 147.9, 135.5, 71.2, 60.1, 46.7, 35.3, 30.4, 29.5, 24.1 20.0.

Synthesis of 2,6-Di-*tert*-butyl-cyclohexadienone-4-oxime (6b). This compound was obtained from the reaction of 2,6-di-*tert*-butyl-4-dimethylaminomethylenephenol (**6**), (3.87 g, 0.015 mol) with nitric oxide as described in the synthesis of **1a**. This reaction also did not yield any precipitate of sodium-2,6-di-*tert*-butyl-cyclohexadienone-4-oximate **(6a)**. The reaction mixture was treated with 0.1 M HCl until no precipitate of **6b** was formed, and the yellow precipitate of **6b** formed was filtered and thoroughly washed with water. The product was recrystallized from methanol/water (1:2). Yield: 2.36 g (68%). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99; N,5.95. Found C, 71.22; H, 8.92; N, 5.84. IR (KBr, cm^{-1}): 1609 (C=O, s). UV−vis (MeOH, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 304 (14 624). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29 (s, 18H), 6.9 (d, 1H), 7.02 (d, 1H), 12.0 (br, s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 187.3, 152.9, 150.8, 150.7, 129.6, 117.3, 36.1, 35.4, 29.7, 29.6.

Crystallographic Data. X-ray diffraction data were collected for single crystals of compounds **(1b), (1c)** and **(5b)** on a P4 Diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1)$ = 0.70926 Å; $\lambda(K\alpha_2)$ = 0.71354 Å] and a graphite monochromator at −100 °C. The crystals were mounted on a glass fiber using epoxy adhesive resin and were coated with Paratone N oil. The intensities of three standard reflections monitored every 100 reflections during the respective data collections indicated negligible crystal decomposition. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using structure solution programs from the SHELXTL system.[35] The data were not corrected for absorption. All hydrogen atoms were located in successive Fourier maps and refined isotropically, whereas the non-hydrogen atoms were refined anisotropically.

Ab Initio Calculations The density functional calculations shown in Figures 1 and 2 were calculated with the Gaussian98 program suite,[36] on a Silicon graphics Origin system. Basis sets and theoretical methods are similar to those described in prior reports.[18]

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Supporting Information Available: Tables of crystallographic data (S1), positional parameters, bond distances and angles, anisotropic displacement parameters and hydrogen atom coordinates for **1b** (S2−S5), **1c** (S6−S9), and **4b** (S10−S13), and IR spectra data (S14). In addition, ORTEP views of **1c** and **5b** are shown in Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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