Catalytic Autoxidation of Benzoquinone Dioximes with Nitrogen Oxides: Steric Effects on the Preparation of Monomeric Dinitrosobenzenes

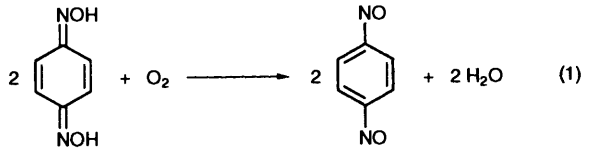
R. Rathore, J. S. Kim and J. K. Kochi *
Chemistry Department, University of Houston, Houston, TX 77204-5641, USA

A convenient catalytic method for the autoxidation of quinone dioximes to dinitrosobenzenes with dioxygen is based on the presence of small amounts of nitrogen oxides. The catalytic cycle is deduced from the facile chemical oxidation of quinone dioxime to dinitrosobenzene with stoichiometric amounts of the 1-electron oxidant, nitrosonium—either as the $NO^+BF_4^-$ salt or the disproportionated ion pair $NO^+NO_3^-$ derived from nitrogen dioxide. The regeneration of NO^+ occurs by the subsequent oxidation of nitric oxide (NO) with dioxygen to nitrogen dioxide followed by the disproportionation to nitrosonium nitrate in the presence of electron-rich donors. Indeed, dioximes of various *p*-benzoquinones are shown to be strong reducing agents by transient electrochemistry. Electrochemical oxidation also leads to dinitrosobenzenes in good yields at anodic potentials of *ca.* 1.3 V. The substitution of *p*-dinitrosobenzene with bulky alkyl groups stabilizes the monomeric form, which is otherwise extensively associated.

Nitroso compounds are of both industrial[1] and theoretical[2] interest. Notably, whilst most organic nitroso compounds are faintly yellow in the solid state, their solutions are bright green or blue.[3] This phenomenon has been attributed to the reversible dimerization of nitroso compounds. Thus, nitrosoarenes exist largely as monomers in solution, whereas they are dimeric in the solid state. The only aromatic nitroso compounds known to be monomeric both in solution and in the solid state are those with strong electron-donating groups (*e.g. N,N*-dimethyl-4-nitrosoaniline).[4] The various factors such as substituent and electronic effects governing the reversible dimerization of nitrosoaromatic compounds have not been generally explored owing to the unavailability of these compounds by convenient synthetic procedures.

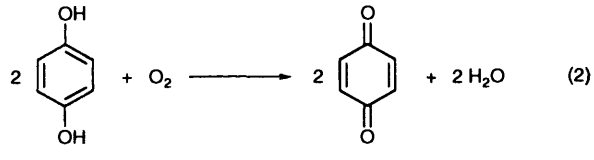
Although a number of nitrosoarenes are known, the corresponding dinitroso derivatives are scarce.[5] Thus, the parent *p*-dinitrosobenzene has been prepared as a polymeric material from *p*-benzoquinone dioxime with oxidants such as ferric chloride,[6] hydrogen peroxide,[7] potassium ferricyanide,[8] nitrogen dioxide,[9] *etc.* In all cases, the reagents are employed in stoichiometric amounts and in strongly acidic aqueous media.

We now report on the electron-donor properties of various quinone dioximes as assessed from transient electrochemistry. The facile electrochemical oxidation of quinone dioximes in conjunction with their low oxidation potentials has led to the development of a procedurally simple catalytic method for the autoxidation of quinone dioximes $Q(NOH)_2$ to dinitrosobenzenes $Ar(NO)_2$ [*i.e.* eqn. (1)].



(1)

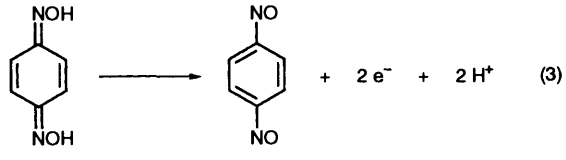
The NO_2-catalysed autoxidation of quinone dioximes to dinitrosobenzenes with dioxygen [eqn. (1)] represents a transformation akin to that of electron-rich hydroquinones to electron-deficient quinones[10] [*i.e.* eqn. (2)].



(2)

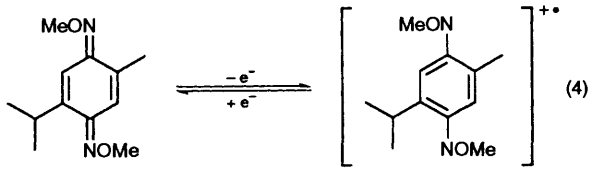
Results

I. *Quinone Dioximes as Electron Donors.*—The substituted *p*-benzoquinone dioximes **1**–**6** (see Table 1) were oxidized electrochemically at a platinum electrode as 2×10^{-3} mol dm^{-3} solutions in acetonitrile containing 0.2 mol dm^{-3} tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. The cyclic voltammograms (CV) of all the quinone dioximes were chemically irreversible (see Fig. 1) at a scan rate of $v = 100$ mV s^{-1} at 25 °C. Only a well-defined anodic current maxima, but no corresponding cathodic wave, was observed, even at scan rates up to $v = 5000$ mV s^{-1}. The (chemically) irreversible peak potentials (E_p) were referenced to saturated calomel electrode (SCE) and calibrated with respect to added ferrocene. The magnitude of the irreversible anodic peak current was consistent with a 2-electron oxidation to the dinitrosobenzenes according to eqn. (3).*



(3)

The dimethyl ether of 2-isopropyl-5-methyl-1,4-benzoquinone dioxime **4** was also oxidized under similar conditions (see Experimental section). Reversible cyclic voltammograms (see Fig. 1) of the dimethyl ether were obtained at scan rates of $v = 25$–100 mV s^{-1}. Each showed the anodic/cathodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) at 25 °C. The calibration of the CV peaks with ferrocene indicated the reversible oxidation potential of ($E_{\frac{1}{2}} = 1.4$ V) for the formation of the cation radical $\mathbf{4}^{\bullet+}$ *via* the 1-electron redox couple [*i.e.* eqn. (4)].



(4)

* (a) Due to the broadening of the irreversible peak potentials of dioximes the calibration of cyclic voltammogram peak current with equimolar ferrocene did not quite show the current equivalent to 2-electron oxidation. (b) Note that the initial electron transfer of quinone dioxime is reversible in strong acid.[11] Compare with the analogous anodic behaviour of H_2Q in ref. 18.

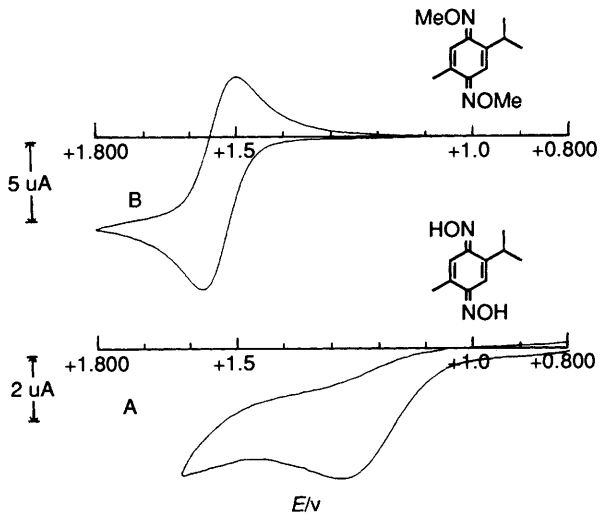
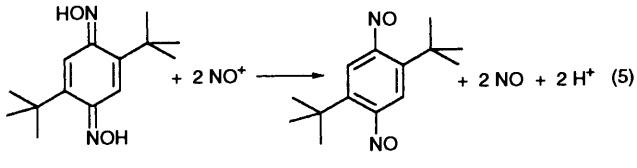


Fig. 1 Cyclovoltammograms for the oxidation of (A) 2-isopropyl-5-methyl-*p*-benzoquinone dioxime **4** (2×10^{-3} mol dm^{-3}) and (B) its dimethyl ether (5×10^{-3} mol dm^{-3}) in acetonitrile containing 0.2 mol dm^{-3} electrolyte (TBAHP) at scan rate $v = 100$ mV s^{-1} at 25 °C

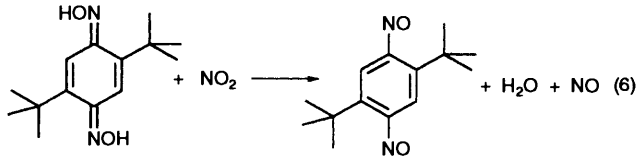
II. *Electrochemical Oxidation of Quinone Dioximes to Dinitrosobenzene.*—The dioxime **6** was electrochemically oxidized by passing an anodic current through an acetonitrile solution (5×10^{-3} mol dm^{-3}) containing 0.1 mol dm^{-3} TBAH. The initially colourless solution immediately turned greenish and progressively became bright green as the bulk electroxidation was carried out at a constant potential of 1.3 V. The solvent was evaporated under reduced pressure and the mixture was dissolved in hexane. The green (hexane) solution was filtered through a short pad of silica gel and simple removal of the solvent from the filtrate afforded the dinitrosobenzene **6** in a quantitative yield according to the stoichiometry in eqn. (3) (see Experimental section).

III. *Stoichiometric Oxidation of Quinone Dioximes with Nitrogen Oxides.*—The redox stoichiometry for the electrochemical transformation of the quinone dioxime to dinitrosobenzene in eqn. (3) was further established by chemical oxidation with either nitrosonium tetrafluoroborate or nitrogen dioxide.

Nitrosonium oxidation. A mixture of the dioxime **6** and 2 equiv. of nitrosonium tetrafluoroborate salt was slurried in dichloromethane at −10 °C under an argon atmosphere. Continued stirring of the heterogeneous mixture for 1 h yielded a dark solution which was allowed to warm up to room temperature. Spectral analysis of the head gas indicated the presence of only nitric oxide. Neutralization of the dichloromethane solution with sodium hydrogen carbonate followed by filtration and evaporation of the solvent furnished the crystalline dinitrosobenzene **6** in 92% yield according to the stoichiometry in eqn. (5).



Nitrogen dioxide oxidation. A suspension of the quinone dioxime **6** in dichloromethane was treated under argon atmosphere with an equimolar amount of nitrogen dioxide at −10 °C. Upon continued stirring, the slurry was transformed into a clear green solution (10 min). Removal of the solvent under reduced pressure led to the dinitrosobenzene **6** in excellent yield. Spectral analysis of the head gas revealed the characteristic (UV) absorptions of nitric oxide with resolved vibrational fine structure at λ_{max}/nm 204, 214 and 222[12] and a diagnostic nitrogen-oxygen stretching frequency (IR)[13] at ν_{NO}/cm^{-1} 1876. The introduction of dioxygen into the IR cell led to the absorption spectrum of nitrogen dioxide[14] (which was clearly absent in the IR spectrum of the head gas) in accordance with the stoichiometry in eqn. (6).

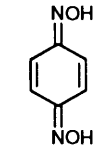
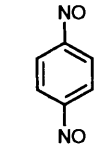
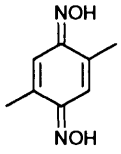
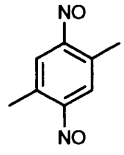
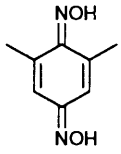
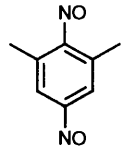
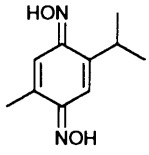
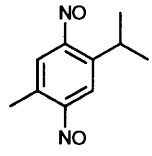
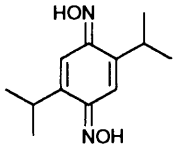
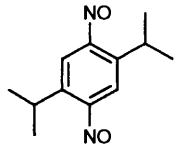
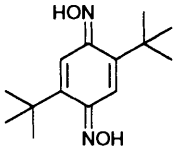
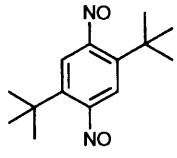


IV. *Catalytic Autoxidation of Benzoquinone Dioximes with Nitrogen Oxides.*—The rapid autoxidation of nitric oxide[15] formed in eqns. (5) and (6) led us to devise a catalytic method for the autoxidation of quinone dioximes to dinitrosobenzenes as follows.

The stirred slurry of the *p*-benzoquinone dioxime **1** (10 mmol) in dichloromethane (100 cm^3) under an oxygen atmosphere turned bright yellow upon the addition of a small amount of nitrogen dioxide (1 mmol) at −10 °C. [Note that no perceptible change in physical appearance or colour was observed in the absence of nitrogen dioxide.] The mixture was warmed to room temperature and stirred overnight to afford a brown suspension. The solid residue was filtered *in vacuo* and washed with hot ethanol to remove the unchanged dioxime. The solid was sublimed *in vacuo* and *p*-dinitrosobenzene (9 mmol) was collected as a green solid using a cold trap (−78 °C). The green (monomeric) solid turned pale yellow on warming to −20 °C. The polymeric material was found to be insoluble in all organic solvents. Spectral analyses of the pale yellow solid showed characteristic IR and UV–VIS absorptions at ν_{NO}/cm^{-1} 1267 and λ_{max}/nm 300, respectively.[5a] The pale yellow solid was further characterized as (polymeric) *p*-dinitrosobenzene by oxidation with *m*-chloroperoxybenzoic acid or trifluoroperoxyacetic acid to *p*-dinitrobenzene in quantitative yield.

With this simple catalytic procedure, a number of the analogous quinone dioximes in Table 1 could be converted into the corresponding dinitrosobenzenes in excellent yields. In order to examine this catalytic autoxidation in detail, we focused our attention on the dioximes **4**, **5** and **6** since they afforded dichloromethane-soluble dinitrosobenzenes. For example, a slurry of the quinone dioxime **4** (2 mmol) in dichloromethane (20 cm^3) was (magnetically) stirred at −10 °C under an oxygen atmosphere for several hours without any perceptible change. When a catalytic amount of nitrogen dioxide (0.2 mmol) was added, the suspension took on a green coloration which upon continued stirring yielded a clear yellow–green solution (~6 h). The solvent was removed under reduced pressure and the crude pale yellow residue was dissolved in hexane. The solution was filtered through a short pad of silica gel column to afford a clear, bright green solution. The removal of the solvent under reduced pressure yielded the dinitrosobenzene **4** as a pale yellow solid, which was essentially free of organic impurities (< 1%) based on spectral (IR, NMR) analyses. The dinitrosobenzene **4** was further characterized by oxidation to the *p*-dinitrobenzene derivative[5b] in quantitative yield using *m*-chloroperoxybenzoic acid. The yield of dinitrosobenzene was thus in excess of ~1000% based on nitrogen dioxide as the added oxidant. The dioximes **5** and **6**

Table 1 Catalytic autoxidation of benzoquinone dioximes to dinitrosobenzenes with nitrogen dioxide

No.	Dioxime $[Q(NOH)_2]$	$(E_p)^a$	$[Q(NOH)_2]^b$ (mmol)	NO_2 (mmol)	Time[c] (h)	Products[d] (%) $[Ar(NO)_2]$
1		(1.30)	10	1.0	10	 (90)
2		(1.27)	10	2.0	4	 (92)
3		(1.14)	8	0.8	4	 (94)
4		(1.24)	10	1.0	3	 (88)
5		(1.30)	2	0.2	1	 (95)
6		(1.33)	3	0.3	2	 (90)

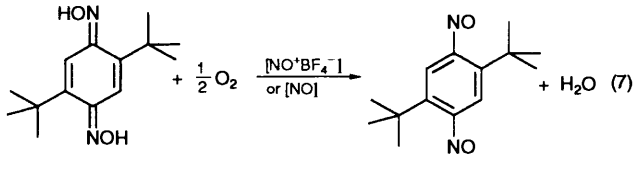
[a] V *vs.* SCE at 25 °C. [b] Dichloromethane (10 cm^3) was used for each mmol of dioxime. [c] See text. [d] Isolated yield.

were similarly oxidized to the corresponding dinitrosobenzenes in excellent yields.

It is noteworthy that 2,5-di-*tert*-butyl-*p*-dinitrosobenzene **6** was obtained as a bright green crystalline solid which was quantitatively oxidized to the corresponding crystalline (pale yellow) dinitrobenzene using trifluoroperoxyacetic acid.

The catalytic autoxidation of quinone dioximes could also be achieved with small amounts of other nitrogen oxides such as nitrosonium salts ($NO^+BF_4^-$) and nitric oxide (NO). For example, the addition of a few crystals of nitrosonium salt (~0.1 equiv. of $NO^+BF_4^-$) to a suspension of the quinone dioxime **6** in dichloromethane under oxygen atmosphere led to dinitrosobenzene **6** in excellent yields according to the stoichiometry in eqn. (7).

The same results were obtained when the autoxidation was performed in the presence of small amounts of nitric oxide.



V. *Spectroscopic Properties of Dinitrosobenzenes in the Solid State and in Solution.*—IR spectra of dinitrosobenzenes **1**–**5** in KBr pellets showed strong characteristic N–O stretching frequencies at ν_{NO}/cm^{-1} 1260–1270. In contrast, the solid-state IR spectrum of 2,5-di-*tert*-butyl-*p*-dinitrosobenzene **6** showed the N–O stretching frequency at ν_{NO}/cm^{-1} 1342. The IR spectrum of the dinitrosobenzene **6** in dichloromethane solution was almost identical with that obtained in the solid state (see

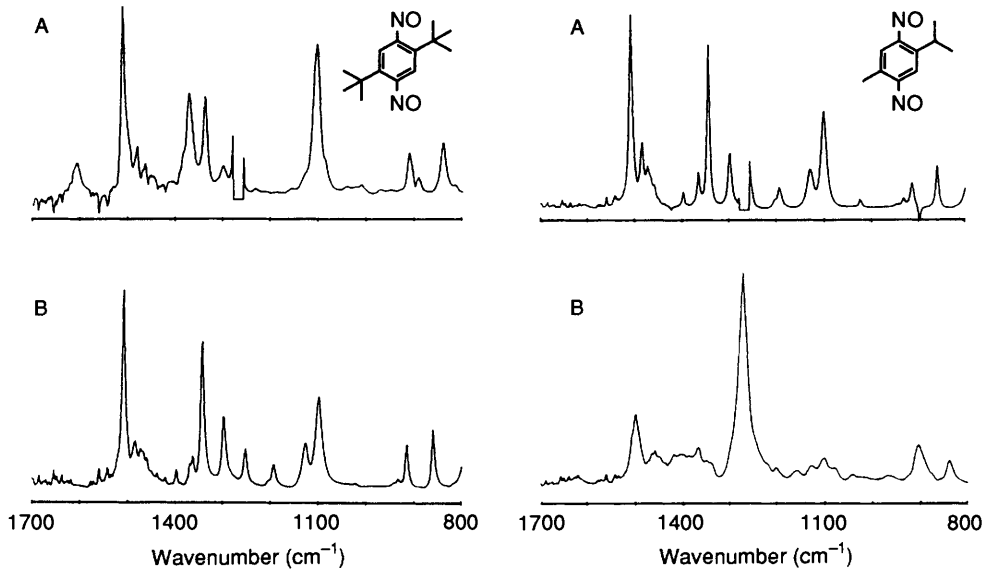


Fig. 2 IR absorption spectra of 2-isopropyl-5-methyl-*p*-dinitrosobenzene **4** and 2,5-di-*tert*-butyl-*p*-dinitrosobenzene **6** in (A) solution (in dichloromethane) and (B) solid state (KBr pellet)

Fig. 2). Interestingly, the IR spectra of the dinitrosobenzenes **4** and **5** in solution showed prominent peaks at 1336 and 1332 cm^{-1}, respectively, and they were quite distinct from those measured in the solid state. For example, the absorption band at 1265 cm^{-1} in the solid-state spectra of both the dinitrosobenzenes **4** and **5** was completely replaced by the bands at 1336 and 1332 cm^{-1}, respectively, in solution (see Fig. 2). The IR spectra of the dinitrosobenzenes **1–3** could not be obtained in solution owing to their poor solubility in dichloromethane.

UV spectra of the solid dinitrosobenzenes **1–6** (on alumina support) were obtained using the diffuse reflectance technique. The dinitrosobenzenes **1–5** showed characteristic absorptions at ~310–380 nm with a nondescript tail extending well beyond 400 nm, whereas 2,5-di-*tert*-butyl-*p*-dinitrosobenzene **6** showed a pair of well resolved bands at λ_{max}/nm 340 and 810. UV spectra of compounds **4–6** in dichloromethane solution showed bands at 350 and 810 nm. It is noteworthy that the solid-state UV spectrum of the dinitrosobenzene **6** was identical with that (bands at 350, 810 nm) in solution. On the other hand, both dinitrosobenzenes **4** and **5** showed the 810 nm band only in solution.

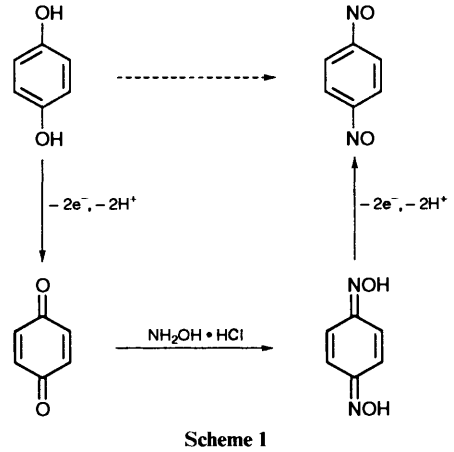
An unusual downfield chemical shift of the methine proton (δ 5.19 ppm) of the isopropyl group and of the methyl group (3.28 ppm) in 2-isopropyl-5-methyl-*p*-dinitrosobenzene **4** and also of the methine protons (5.17 ppm) of the two symmetrical isopropyl groups in 2,5-diisopropyl-*p*-dinitrosobenzene **5** was observed. In order to examine the origin of this unusual chemical shift of the methine protons of the isopropyl groups in the nitrosobenzenes **4** and **5**, a comparison of the chemical shifts of the methine and methyl protons was made with those of the dimethoxy and dinitro analogues of **4** and **5**. The NMR chemical shifts are summarized in Table 2.

It is interesting to note that the chemical shift of the 2-methyl protons (3.21 ppm) in 2,4,5-trimethylnitrosobenzene was also significantly shifted downfield when compared to the shift of 2,6-dimethyl protons (2.33 ppm) in nitrosomesitylene.[16] The anisotropic deshielding effect is evidently more pronounced in 2,4,5-trimethylnitrosobenzene, probably owing to the nitroso group being in plane. On the other hand, it was absent in nitrosomesitylene consistent with the nitroso group being out of the aromatic plane.*

Discussion

Quinone Dioximes as Reducing Agents.—Transient electrochemical studies reveal that benzoquinone dioximes are excellent reducing agents[17] (E_p = ~1.3 V *vs.* SCE), in spite of the fact that they are derivatives of quinones which are well-known oxidants. Indeed, the electrochemical behaviour of the dioximes in acetonitrile solution parallels that of hydroquinones.[18] (In this regard, quinone dioximes are better considered to be 'iminylogues' of hydroquinones.) Furthermore, the dimethyl ether of the dioxime **4** shows a reversible cyclic voltammogram (see Fig. 1) with an oxidation potential ($E_{\frac{1}{2}}$/V 1.45) comparable to that of the hydroquinone dimethyl ether ($E_{\frac{1}{2}}$/V 1.35).

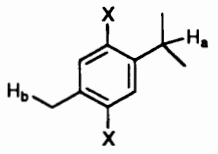
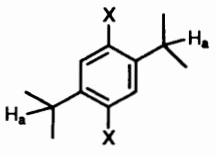
Formally, the oxidation of the quinone dioximes to the dinitrosobenzenes involves the removal of two electrons and two protons. This redox stoichiometry is clearly established in eqn. (3) by quantitative electrochemical oxidation of the dioxime **6** in acetonitrile to the dinitrosobenzene **6**. It should be noted that the 2-electron oxidation of hydroquinone to quinone followed by a functional group interconversion of quinone to dioxime and subsequent 2-electron oxidation corresponds to an overall conversion of 1,4-dihydroxybenzene (hydroquinone) into 1,4-dinitrosobenzene as illustrated in Scheme 1.



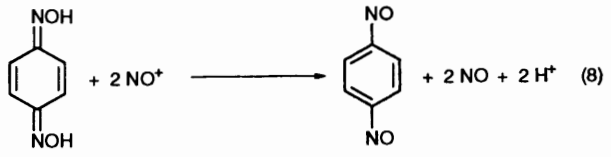
Scheme 1

* The unusual chemical shift of the isopropyl methine and methyl protons in 2-alkyl substituted nitrosobenzenes is, probably, due to the anisotropic deshielding effect of the coplanar nitroso group (with aromatic plane).

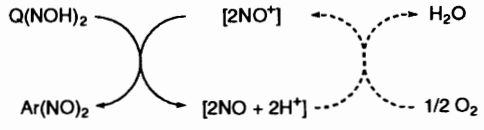
Table 2

	X	H_a (δ)	H_b (δ)		X	H_a (δ)
	NO	5.19	3.28		NO	5.17
	NO_2	3.36	2.61		NO_2	3.29
	OMe	3.22	2.12		OMe	3.30

Catalytic Autoxidation of Quinone Dioximes to Dinitrosobenzenes with Nitrogen Oxides.—The redox stoichiometry for the transformation of the dioxime to dinitrosobenzene in eqn. (3) is further established by chemical oxidation with nitrosonium *via* a pair of 1-electron reduction steps involving the conversion of nitrogen(III) to nitrogen(II) [*i.e.* see eqn. (8)].

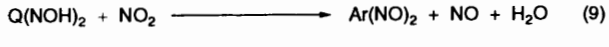


This together with the subsequent reoxidation of nitric oxide by dioxygen (which is known to be rapid)[15] can constitute the requisite reduction/oxidation for the catalytic autoxidation with NO^+, as described in eqn. (7). Accordingly, the stoichiometric reaction in eqn. (5) and the schematic regeneration of NO^+ with dioxygen are represented by solid and dashed arrows, respectively, in Scheme 2.

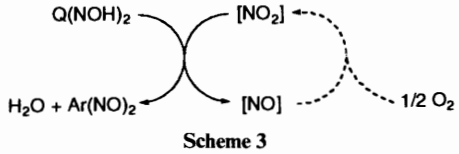


Scheme 2

In a similar way, the stoichiometric oxidation of quinone dioxime with nitrogen dioxide [see eqn. (6)] represents an alternative oxidation of quinone dioxime *via* the 2-electron reduction of nitrogen(IV) to nitrogen(II) in a single step [*i.e.* see eqn. (9)].

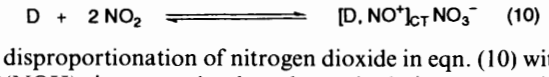


This transformation in combination with the reoxidation of nitric oxide with dioxygen constitutes the catalytic cycle in Scheme 3 for the catalytic autoxidation with NO_2, as described in eqn. (7). (The solid and dashed arrows have the significance described above.)



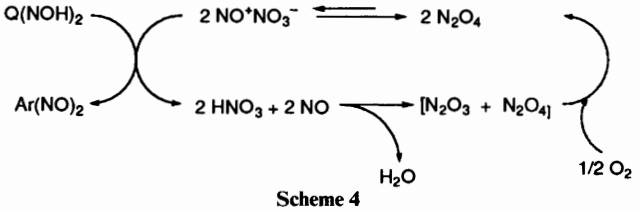
Scheme 3

The two catalytic cycles presented in Schemes 2 and 3, though seemingly unrelated, can be viewed in a unified way by invoking the ready interconversion of NO^+ and NO_2. Thus previous studies showed that NO^+ is spontaneously generated by the disproportionation of nitrogen dioxide (NO_2) in the presence of electron-rich donors (D) [*i.e.* eqn. (10)].[19]



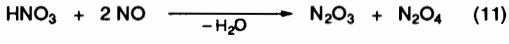
Such a disproportionation of nitrogen dioxide in eqn. (10) with D = $Q(NOH)_2$ is expected to be enhanced relative to that with D = hexamethylbenzene,[19] owing to the lower oxidation potentials of quinone dioximes.

Based on this understanding, we propose that the oxidation of quinone dioxime with nitrogen dioxide proceeds *via* a disproportionated ion pair, nitrosonium nitrate (see Scheme 4).



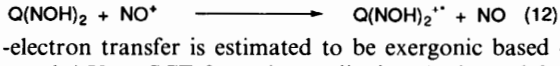
Scheme 4

Thus, 2 equiv. of nitrosonium nitrate and 1 equiv. of dioxime are converted into 2 equiv. each of nitric acid and nitric oxide and 1 equiv. of dinitrosobenzene. Such a mixture of nitric acid and nitric oxide is metastable, undergoing rapid transformation to dinitrogen trioxide and dinitrogen tetraoxide with liberation of water [*i.e.* eqn. (11)].[20]



Since dinitrogen trioxide is in reversible equilibrium with NO and NO_2,[21] it is readily converted into N_2O_4 (NO_2) in the presence of dioxygen. Thus, a complete catalytic cycle of the NO_2 catalysed autoxidation of dioxime to dinitrosobenzene corresponds to that presented in Scheme 4. (This catalytic cycle is reminiscent of the mechanism presented earlier for the autoxidation of hydroquinones to quinones.)[10]

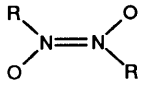
The complex equilibria amongst various nitrogen oxides in Scheme 4 are the building blocks in the catalytic cycle for the autoxidation of quinone dioximes to dinitrosobenzenes. Importantly, the effective oxidizing agent for the dioxime is NO^+ [see eqn. (5)]—the other nitrogen oxides being primarily involved in the reoxidation part of the catalytic cycle. Thus, the overall 2-electron oxidation of dioxime to dinitrosobenzene by 2 equiv. of NO^+ proceeds most likely *via* successive 1-electron oxidation steps.* Although the alternative 2-electron mechanism for the dioxime oxidation cannot be ruled out, we note that the direct electrochemical oxidation of dioxime to dinitrosobenzene in eqn. (3) yields 2 equiv. of electrons. In such a process, the catalytic efficiency depends upon the effectiveness of initial electron transfer from the quinone dioxime to NO^+ [*i.e.* eqn. (12)] followed by the rapid proton loss. The driving force for



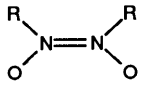
the 1-electron transfer is estimated to be exergonic based on E_{ox}° = ~1.4 V *vs.* SCE for quinone dioxime (estimated from the E° of corresponding dimethyl ether) and E_{red}° = 1.5 V *vs.* SCE for nitrosonium in dichloromethane.[22]

* In the 1-electron mechanism, the quinone dioxime cation radical [$Q(NOH)_2^{\bullet+}$] is a highly transient species and undergoes a rapid proton loss to afford the radical [HNOQNO$^{\bullet}$]. The subsequent (fast) electron-transfer generates the cation [$HNOQNO^+$] which by rapid proton loss leads to the dinitrosobenzene. Compare with the analogues ECE mechanism for hydroquinone oxidation to quinone as delineated by Hammerich and Parker in ref. 18.

Dimeric Versus *Monomeric Dinitrosobenzenes.*—Reversible dimerization of nitroso compounds is a well-known process.[23] In fact, most organic nitroso compounds exist as colourless or pale yellow dimers in the solid state and as green or blue monomeric species in solution (or pure liquid state). X-Ray crystallography[24] of a number of dimeric nitroso compounds indicates that the planar azo dioxide structure exists as *cis* and *trans* isomers, *i.e.* **I** and **II**.



I



II

It is noteworthy that most dimeric aromatic nitroso compounds (*i.e.* azo dioxides) are found to exist in the *trans* configuration. Exceptions to this general rule are the dimeric nitrosobenzene and α-nitrosonaphthalene which favour the *cis* configuration.[24a]

It should be noted that the green colour (*i.e.* a broad UV–VIS band at 800–810 nm) coupled with IR absorption at 1330–1350 cm^{-1} serves as a diagnostic feature of monomeric nitroso compounds. By comparison, dimeric colourless compounds (UV–visible band at 300–380 nm) show an IR stretching frequency at 1260–1270 cm^{-1}.

There is little known about the monomeric or dimeric (polymeric) nature of *p*-dinitrosobenzenes.[23b] It has been suggested by Ruggli and Bartusch[25] that *p*-dinitrosobenzene **1** exists, at room temperature, as a colourless insoluble polymeric solid (1263 cm^{-1}) compared to nitrosobenzene dimer (1265 cm^{-1}) which readily yields monomer in nonpolar solvents.[4] The methyl substituted (polymeric) dinitrosobenzenes **2** and **3** are poorly soluble in dichloromethane but can be readily sublimed to green monomers at −78 °C. They turned pale yellow (polymeric form) on warming to −10 °C.

Substitution of the parent dinitrosobenzene with a sterically hindering isopropyl group(s), affords readily soluble forms of the dinitrosobenzenes **4** and **5** which show characteristic spectral features of the monomeric and dimeric nitrosobenzenes in solution and solid states, respectively. Furthermore, the replacement of the isopropyl groups in **5** by bulkier *tert*-butyl groups results in the first synthesis of dinitrosobenzene **6** which exists as monomeric species even in the solid state (bright green crystalline solid). The *tert*-butyl substituted dinitrosobenzene **6** exhibits the characteristic spectral features (IR and UV) typical of monomeric nitrosobenzene in both solution and the solid state.

Summary and Conclusions.—We have demonstrated that the dioximes of various *p*-benzoquinones are strong reducing agents. The efficient anodic oxidation of the quinone dioximes to the corresponding dinitrosobenzenes occurs by the uptake of 2 equiv. of electrons. In addition, a facile catalytic method has been developed for the oxidation of dioximes to dinitrosobenzenes with dioxygen in the presence of catalytic amounts of nitrogen oxides (NO_x) at room temperature or below. The catalytic cycle has been deduced from the facile oxidation of dioxime to dinitrosobenzene with stoichiometric amounts of the 1-electron oxidant, nitrosonium—either as the $NO^+BF_4^-$ salt or the disproportionated ion pair $NO^+NO_3^-$ derived from nitrogen dioxide. The regeneration of NO^+ occurs by the subsequent oxidation of nitric oxide (NO) with dioxygen to nitrogen dioxide followed by the disproportionation to nitrosonium nitrate. The efficient interconversion of different nitrogen oxides NO_x = NO, NO_2, NO^+ and NO_3^- coupled with stepwise oxidation of the dioxime *via* a successive 1-electron/proton transfers forms the critical component of the catalytic cycle.

Substitution of *p*-dinitrosobenzene with bulky *tert*-butyl groups (*e.g.* 2,5-di-*tert*-butyl-*p*-dinitrosobenzene) stabilizes the monomeric form even in the crystalline state.

Experimental

Materials.—Nitrogen dioxide (Aldrich) was purified according to Addison's procedure.[26] Solutions of nitrogen dioxide in anhydrous dichloromethane were prepared volumetrically and stored in Schlenk tubes (equipped with a Teflon vacuum stopcock) in the refrigerator. Nitrosonium tetrafluoroborate (Strem) was stored in a Vacuum Atmospheres HE-493 dry box kept free of oxygen, moisture and solvent vapours. Tetrabutylammonium hexafluorophosphate (Aldrich) was used as received. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~20% by volume) until the acid layer remained clear. After separation, it was washed successively with water, aqueous sodium hydrogen carbonate, water and brine and then dried ($CaCl_2$). Dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. Acetonitrile (Fischer) was stirred with $KMnO_4$ for 24 h and the mixture was refluxed until colourless. The MnO_2 was filtered off, and the acetonitrile was distilled from P_2O_5 under an argon atmosphere, and then refluxed over CaH_2 for 6 h. After distillation from CaH_2, the solvent was stored in a Schlenk flask under an argon atmosphere. *p*-Benzoquinone dioximes were prepared from quinone monoximes and hydroxylamine hydrochloride in ethanol. The quinone monoximes were readily available from quinones and hydroxylamine hydrochloride in ethanol[27] or from the nitrosation of the corresponding phenols[28] using standard literature methods. Commercially available 2,6-dimethylphenol, 3,5-dimethylphenol, thymol and 2,5-di-*tert*-butylhydroquinone (Aldrich) were used without further purification. 2,5-Di-*tert*-butylbenzoquinone was prepared by catalytic autoxidation of corresponding hydroquinone (Aldrich).[10] Hydroxylamine hydrochloride, methoxylamine hydrochloride, *m*-chloroperoxybenzoic acid and trifluoroacetic acid (Aldrich) were used as received.

Instrumentation.—The UV–VIS absorption spectra were recorded on a Perkin-Elmer model 330 spectrophotometer. Solid samples for diffuse reflectance spectra were prepared by diluting the sample (1.6% w/w) with alumina. IR spectra were recorded on a Nicolet 10 DX FT spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer and chemical shifts are reported in ppm units downfield from tetramethylsilane. Gas chromatography was performed on a Hewlett-Packard 5890A series FID gas chromatograph fitted with a 3392 integrator. GC–MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV).

Cyclic Voltammetry of Quinone Dioximes.—Cyclic voltammetry (CV) was performed on a BAS 100A Electrochemical Analyser. The CV cell was of an airtight design with high vacuum stopcocks, Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1 mm^2) significantly. The SCE reference electrode and its salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of a

platinum gauze that was separated from the working electrode by ~3 mm.

The CV measurements were carried out in a solution of 0.2 mol dm^{-3} supporting electrolyte (tetrabutylammonium hexafluorophosphate) and 2×10^{-3} mol dm^{-3} dioximes or 5×10^{-3} mol dm^{-3} dioxime *O*-dimethyl ether in dry acetonitrile under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 100 mV s^{-1} and were IR compensated. The potentials were referenced to SCE and calibrated with added ferrocene (5×10^{-3} mol dm^{-3}). The oxidation potential ($E_{\frac{1}{2}}$) values were calculated by taking the average of the anodic and cathodic peak potentials.

Preparative-scale Electrolysis of Quinone Dioximes.—The electrooxidations were carried out with a PAR Model 173 potentiostat/galvanostat equipped with PAR Model 179 digital coulometer which provided a feed-back compensation for ohmic drop between working and the reference electrodes. The voltage-follower amplifier (PAR Model 178) was mounted external to the potentiostat with a minimum length of high-impedance connection to the reference electrode. The electrochemical cell was of airtight design with high vacuum. The counter electrode was constructed of a double coil of Nichrome wire with a large surface area. The working electrode consisted of a platinum-wire cage wrapped with a platinum gauze with a total surface area of ~1.1 cm^3. The electrooxidations were carried out at a constant potential.

General procedure. The dioxime **6** (50 mg, 0.2 mmol) was dissolved in acetonitrile (50 cm^3) containing 0.1 mol dm^{-3} electrolyte (TBAPH). This mixture was placed in the centre compartment of the electrochemical cell. The reference electrode and counter electrode compartments were charged with the acetonitrile containing 0.1 mol dm^{-3} electrolyte. The mixture was electrolysed at a constant potential of 1.3 V for 1.5 h. The current flowed was recorded by the digitized coulometer to be 11.0 C during this period. The current flow was stopped at the end of this period due to the mechanical clogging of the frits. The green reaction mixture was collected in a flask and the solvent was removed under reduced pressure. The green residue was suspended in hexane and filtered through a short pad of silica gel to afford the green crystalline dinitrosobenzene **6** in quantitative yield (14 mg, 0.056 mmol) based on the passage of the current.

Synthesis of 2,5-*Diisopropyl*-p-*benzoquinone.*—Owing to the difficulty in preparing 2,5-diisopropyl-*p*-benzoquinone from the only known literature procedure,[27] we developed an efficient method for the preparation of 2,5-diisopropyl-1,4-dimethoxybenzene as described below. The dimethoxybenzene was readily converted into the desired quinone by oxidation with ceric ammonium nitrate.[29] To a solution of 1,4-dimethoxybenzene (13.8 g, 0.1 mol) dissolved in a minimum of isopropyl alcohol (15 cm^3) was added conc. sulfuric acid (100 cm^3) under an argon atmosphere. The reaction mixture turned deep orange upon addition of the sulfuric acid. The orange mixture was set aside for 12 h with occasional shaking. The reaction mixture was later poured over ice (1000 g). The aqueous layer was extracted with diethyl ether and the extract washed with water (3×100 cm^3) followed by aqueous sodium hydrogen carbonate (2×50 cm^3). The organic layer was dried ($MgSO_4$), filtered and evaporated to afford an orange liquid which was distilled *in vacuo*. The distillate was dissolved in ethanol and the solution stored in a freezer to afford crystalline 2,5-diisopropyl-1,4-dimethoxybenzene (17.7 g, 80%); m.p. 45–46 °C; $\delta_H(CDCl_3)$ 1.21 (6 H, d), 1.25 (6 H, d), 3.33 (2 H, m), 3.71 (1 H, s), 3.80 (1 H, s), 6.64 (1 H, s) and 6.75 (1 H, s); δ_C 23.01, 24.33, 26.64, 26.72, 56.96, 109.77, 134.99, 142.92, 148.86, 151.09 and 156.33; *m/z* 222 (M^+). The 2,5-diisopropyl-1,4-dimethoxybenzene (5.6 g, 25 mmol) was oxidized using ceric ammonium nitrate[29] to the corresponding quinone (4.6 g, 95%); m.p. 42–43 °C (lit.,[27] m.p. 42–43 °C); ν_{max}(KBr)/cm^{-1} 2967, 1665vs, 1607, 1463, 1381, 1306, 1238, 1067 and 916; $\delta_H(CDCl_3)$ 1.10 (12 H, d), 2.97 (2 H, m), 6.42 (1 H, s) and 6.46 (1 H, s); δ_C 21.37, 26.34, 129.62, 154.16 and 187.89; *m/z* 192 (M^+).

Synthesis of 2-*Isopropyl*-5-*methyl*-p-*benzoquinone Dioxime Dimethyl Ether.*—A mixture of 2-isopropyl-5-methyl-*p*-benzoquinone[28] (3.0 g, 18.3 mmol) and methoxylamine hydrochloride (4.5 g, 55.0 mmol) in ethanol (50 cm^3) was refluxed for 24 h. The solvent was removed under reduced pressure and the crude reaction mixture was diluted with a mixture of water (100 cm^3) and ethyl acetate (100 cm^3). The organic layer was separated, washed with aqueous sodium hydrogen carbonate (3×50 cm^3), dried ($MgSO_4$), filtered and evaporated under reduced pressure to afford a pale yellow oil. Further purification of the oil by column chromatography on silica gel with ethyl acetate–hexane (1:10) yielded the title compound as a colourless oil (3.55 g, 87%); ν_{max}(neat)/cm^{-1} 2960, 2940, 2817, 1580, 1463, 1258, 1060, 1012, 916, 889 and 862; $\delta_H(CDCl_3)$ 1.10 (6 H, d), 1.99 (2 H, m), 3.15 (1 H, m), 3.93 (3 H, s), 3.94 (3 H, s) and 6.89 (2 H, s); δ_C 17.28, 22.48, 27.02, 62.62, 112.20, 116.53, 137.32, 147.35, 148.77 and 150.58; *m/z* 222 (M^+).

Synthesis of p-*Benzoquinone Monoximes.*—Quinone monoximes were prepared either by nitrosation of the phenols (Method A)[28] or by the reaction of the corresponding quinones with hydroxylamine hydrochloride (Method B).[27]

Method A. To a solution of thymol (15 g, 0.1 mol) in 95% ethanol (150 cm^3) in a 1-dm^3 flask equipped with a mechanical stirrer, was added conc. hydrochloric acid (150 cm^3). This mixture was cooled in an ice–salt bath whilst sodium nitrite (10.3 g, 0.15 mol) was added in portions (~1.0 g) to it with vigorous stirring; during this, the mixture became a green viscous paste. It should be noted that the use of the mechanical stirrer was necessary to maintain the vigorous stirring for 3 h at room temperature. The reaction mixture was poured over a mixture of ice–water (2 dm^3), after which the brown solid was filtered off and washed with water (3×300 cm^3). The brown filter cake was dissolved in a mixture of ethyl acetate (300 cm^3) and water (300 cm^3) and the organic layer was separated, washed with aqueous sodium hydrogen carbonate (3×200 cm^3) followed by brine (3×200 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to yield a light brown solid. The crude solid was suspended in hexane (300 cm^3) and the suspension heated to boiling. The undissolved residue was filtered off and washed with warm hexane to afford 2-isopropyl-5-methyl-*p*-benzoquinone 4-oxime as a pale yellow powder (14.6 g, 82%).

Method B. To a solution of 2,5-di-*tert*-butyl-*p*-benzoquinone (3.0 g, 13.6 mmol) in ethanol (50 cm^3) was added hydroxylamine hydrochloride (2.82 g, 40.0 mmol). The mixture was refluxed for 24 h and ethanol was removed under reduced pressure. The brown residue was worked up as described in Method A to afford 2,5-di-*tert*-butyl-*p*-benzoquinone monoxime (2.30 g, 72%) as a pale yellow powder. Characteristic spectral data of the monoximes are as follows. 2,5-Dimethyl-*p*-benzoquinone 4-oxime (72%), m.p. 172–173 °C (lit.,[28b] 175–176 °C); ν_{max}(KBr)/cm^{-1} 3180, 3070, 2906, 2790, 2373, 1642vs, 1580, 1435, 1402, 1066, 1045, 903 and 780; $\delta_H(CD_3SOCD_3)$ 1.91 (3 H, s), 2.15 (3 H, s), 6.29 (1 H, s), 7.57 (1 H, s) and 13.33 (1 H, s); δ_C 15.47, 16.64, 121.12, 127.50, 138.11, 146.55, 149.26 and 186.58. 2,6-Dimethyl-*p*-benzoquinone 4-oxime (83%), m.p. 186–187 °C (lit.,[28b] 185–186 °C); ν_{max}(KBr)/cm^{-1} 3181, 3070, 2906, 2790, 2373, 1641vs, 1580, 1436, 1402, 1327, 1067, 1046, 903 and 780; $\delta_H(CD_3SOCD_3)$ 2.30 (6 H, s), 6.25 (2 H, s) and 13.00 (1 H, br s). 2-Isopropyl-5-methyl-*p*-benzoquinone 4-oxime (94%), m.p.

159–160 °C (lit.,[28a] 160–164 °C); ν_{max}(KBr)/cm^{-1} 3186, 3070, 2967, 2919, 2851, 2796, 1641vs, 1607, 1580, 1443, 1381, 1245, 1053, 1012, 999, 910 and 848; δ_H(CD_3SOCD_3) 1.16 (6 H, d), 2.20 (3 H, s), 3.20 (1 H, s), 6.36 (1 H, s), 7.57 (1 H, s) and 10.30 (1 H, br s); δ_C 16.96, 21.71, 26.72, 118.33, 129.50, 145.78, 149.33 and 187.88. 2,5-Diisopropyl-*p*-benzoquinone monoxime (81%), m.p. 170 °C (lit.,[27] 172 °C); ν_{max}(KBr)/cm^{-1} 3219, 2960, 1607, 1559, 1265, 1019 and 923; δ_H(CD_3COCD_3) 1.10 (6 H, d), 1.15 (6 H, d), 3.04 (2 H, m), 6.93 (1 H, s) and 7.54 (1 H, s); δ_C 22.44, 27.07, 118.47, 131.43, 148.28, 148.53, 150.62 and 150.93; *m/z* 208 (M^+). 2,5-Di-*tert*-butyl-*p*-benzoquinone monoxime, m.p. 200–201 °C; ν_{max}(KBr)/cm^{-1} 3180, 3069, 2906, 2790, 2373, 1640vs, 1579, 1435, 1400, 1328, 1066, 1046, 902 and 780; δ_H(CD_3SOCD_3) 1.28 (9 H, s), 1.36 (9 H, s), 6.23 (1 H, s), 7.77 (1 H, s) and 12.23 (1 H, s); δ_C 28.91, 30.59, 120.60, 127.60, 147.79, 149.34, 154.86 and 187.87.

Synthesis of Quinone Dioximes.—General procedure. To a solution of 2,5-di-*tert*-butyl-*p*-benzoquinone monoxime (4.0 g, 17 mmol) in ethanol (100 cm^3) was added hydroxylamine hydrochloride (2.4 g, 35 mmol). The mixture was refluxed for 10 h and then cooled to room temperature. The brown precipitate was filtered off and washed with water (3 × 50 cm^3) and cold ethanol (2 × 50 cm^3). The solid was recrystallized from 70% ethanol to afford the dioxime **6** as a pale yellow powder (1.78 g, 42%). The characteristic spectral data are as follows. 2,5-Dimethyl-*p*-benzoquinone dioxime **2** (71%), m.p. 220 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3234, 3144, 2975, 1586, 1463, 1381, 971vs, 882, 854, 752, 664 and 634; δ_H(CD_3SOCD_3) 2.04 (3 H, s), 6.99 (1 H, s), 7.57 (1 H, s) and 11.98 (1 H, s); δ_C 17.30, 115.30, 136.83 and 150.02. 2,6-Dimethyl-*p*-benzoquinone dioxime **3** (80%), m.p. 172 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3233, 2975, 1586, 1463, 1381, 972vs, 883, 854, 754, 664 and 634; δ_H(CD_3SOCD_3) 1.95 and 1.99 (3 H, two singlet, mixture of *cis* and *trans*), 2.30 and 2.34 (3 H, two singlet, mixture of *cis* and *trans*), 6.27 and 6.37 (1 H, two singlet, mixture of *cis* and *trans*), 6.80 and 6.88 (1 H, two singlet, mixture of *cis* and *trans*) and 12.07 (2 H, two singlet, mixture of *cis* and *trans*); δ_C 18.86, 19.47, 24.17, 24.85, 114.67, 118.30, 124.02, 128.63, 130.44, 133.55, 136.00, 139.79, 148.92, 149.11, 149.56 and 149.86. 2-Isopropyl-5-methyl-*p*-benzoquinone dioxime **4** (80%), m.p. 210 °C (decomp.) (lit.,[5b] 200 °C); ν_{max}(KBr)/cm^{-1} 3234, 3145, 2974, 1586, 1463, 1429, 1381, 1265, 1149, 971vs, 882, 855, 752, 664 and 634; δ_H(CD_3SOCD_3) 1.10 (6 H, d), 2.02 (3 H, s), 3.12–3.21 (1 H, m), 7.01 (2 H, d) and 11.97 (2 H, d); δ_C 17.18, 22.31, 26.52, 111.10, 115.58, 136.42, 146.65, 148.52 and 150.19. 2,5-Diisopropyl-*p*-benzoquinone dioxime **5** (76%), m.p. 192 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3247, 3135, 3001, 2959, 2875, 1637, 1581, 1461, 1384, 1264, 983vs, 892, 857 and 765; δ_H(CD_3SOCD_3) 1.07 (12 H, d), 3.09–3.18 (2 H, m), 6.99 (2 H, s) and 11.98 (2 H, s); δ_C 22.34, 26.49, 111.44, 146.19 and 148.68; *m/z* 222 (M^+). 2,5-Di-*tert*-butyl-*p*-benzoquinone dioxime **6**, m.p. 220 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3268, 3125, 2967, 1573, 1368, 1272, 964vs, 875 and 807; δ_H(CD_3SOCD_3) 1.27 (18 H, s), 7.15 (2 H, s) and 11.87 (2 H, s); δ_C 30.13, 35.42, 113.59, 145.93 and 149.28; *m/z* 250 (M^+).

Catalytic Autoxidation of Quinone Dioximes.—The quinone dioxime **1–3** were oxidized to the insoluble polymeric dinitrosobenzenes using Method A, whereas the soluble dinitrosobenzene **4–6** were prepared using Method B.

Method A. A slurry of *p*-benzoquinone dioxime (1.38 g, 10.0 mmol) in dichloromethane (100 cm^3) at −10 °C was stirred under an oxygen atmosphere. To this suspension a pre-chilled solution of nitrogen dioxide in dichloromethane (0.2 mol dm^{-3}; 5 cm^3, 1 mmol) was added. The suspension immediately took on a bright yellow coloration. The mixture was warmed to room temperature and stirred overnight to afford a brown suspension. The brown residue was filtered off and washed with hot ethanol to remove the unchanged dioxime. The pale yellow solid was sublimed at 95–120 °C (0.05 mmHg) as a bright green solid collected on a cold finger cooled by solid CO_2–acetone. The green solid on warming to −20 °C turned pale yellow; it was practically insoluble in organic solvents (1.22 g, 9 mmol, 90%). The characteristic spectral data are as follows. *p*-Dinitrosobenzene **1**, m.p. 210 °C (decomp.) (lit.,[5a] 174–175 °C); ν_{max}(KBr)/cm^{-1} 1484, 1419, 1305, 1264vs (N–O stretch), 1106, 1012, 859, 775, 569 and 482; λ_{max}(solid)/nm 380. 2,5-Dimethyl-*p*-dinitrosobenzene **2**, m.p. 132 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1531, 1498, 1457, 1269vs, 1191, 1043, 894, 848 and 731; λ_{max}(solid)/nm 290. 2,6-Dimethyl-*p*-dinitrosobenzene **3**, m.p. 185 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1531, 1498, 1457, 1269vs, 1191, 1043, 894, 848 and 731; λ_{max}(solid)/nm 310.

Method B. The procedure is similar to that described in the previous method. After being stirred for 3 h at room temperature, the suspension turned into a clear yellow–green solution which, after solvent removal under reduced pressure, furnished a pale yellow solid. This crude product was purified on a short silica gel column with ethyl acetate–hexane (1:20) as an eluent to provide 2-isopropyl-5-methyl-*p*-dinitrosobenzene (95% yield) as a pale yellow solid. The characteristic spectral data in the solid and solution state are as follows. 2-Isopropyl-5-methyl-*p*-dinitrosobenzene **4**, m.p. 180 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3439, 2967, 1498, 1265vs, 1101, 903 and 843; ν_{max}-(CH_2Cl_2)/cm^{-1} 2965, 1609, 1510vs, 1481, 1370, 1336, 1101, 907 and 838; λ_{max}(solid)/nm 300; λ_{max}(CH_2Cl_2)/nm 350 (ε 334) and 810 (ε 46); δ_H($CDCl_3$) 1.48 (6 H, d), 3.28 (3 H, s), 5.19 (1 H, m,), 6.06 (1 H, s) and 6.47 (1 H, s); δ_C 16.99, 24.07, 27.53, 107.87, 110.28, 139.25, 150.22, 159.60 and 161.18. 2,5-Diisopropyl-*p*-dinitrosobenzene **5**, m.p. 140 °C (decomp.); ν_{max}-(KBr)/cm^{-1} 2968, 2931, 2875, 1265vs, 1073, 901 and 831; ν_{max}(CH_2Cl_2)/cm^{-1} 2972, 1605, 1510vs, 1480, 1462, 1376, 1332, 1102, 910 and 822; λ_{max}(solid)/nm 320 and 800; λ_{max}(CH_2Cl_2)/nm 360 (ε 244) and 810 (ε 40); δ_H($CDCl_3$) 1.46 (12 H, d), 5.17 (2 H, m) and 6.21 (2 H, d); δ_C 24.03, 27.50, 105.93, 149.91 and 160.37. 2,5-Di-*tert*-butyl-*p*-dinitrosobenzene **6**, m.p. 220 °C (decomp.) (Found: C, 67.6; H, 8.1; N, 11.3. $C_{14}H_{20}N_2O_2$ requires C, 67.70; H, 8.12; N, 11.29%); ν_{max}(KBr)/cm^{-1} 2994, 2959, 2868, 1510vs, 1342, 1300, 1250, 856 and 786; ν_{max}(CH_2Cl_2)/cm^{-1} 2967, 1605, 1507vs, 1342vs, 1100, 912, 856 and 793; λ_{max}(solid)/nm 330 and 810; λ_{max}(CH_2Cl_2)/nm 810 (ε 63); δ_H($CDCl_3$) 1.46 (12 H, d), 5.17 (2 H, m) and 6.21 (2 H, d); δ_C 24.03, 27.50, 105.93, 149.91 and 160.37; *m/z* 248 (M^+).

Oxidation of p-*Dinitrosobenzenes to* p-*Dinitrobenzenes.*—Dinitrosobenzenes were oxidized with either *m*-chloroperoxybenzoic acid (Method A) or trifluoroperoxyacetic acid (Method B).

Method A. A slurry of *p*-dinitrosobenzene (50.0 mg, 0.36 mmol) and *m*-chloroperoxybenzoic acid (85% technical grade; 189 mg, 1.10 mmol) in dichloromethane (10 cm^3) was stirred at 25 °C under an argon atmosphere for 10 h. A homogeneous solution thus obtained was washed with saturated aqueous sodium hydrogen carbonate (3 × 20 cm^3). The organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure to afford a pale yellow solid. Recrystallization of this from diethyl ether–hexane (1:2) afforded *p*-dinitrobenzene (50 mg, 80%) as a white crystalline solid.

Method B. To a cooled (0 °C) solution of *p*-dinitrosobenzene (50.0 mg, 0.36 mmol) in trifluoroacetic acid (5 cm^3) was added dropwise aqueous 30% hydrogen peroxide (1 cm^3) over a period of 20 min. After being stirred at room temperature for 10 h, the reaction mixture was diluted with cold water (50 cm^3) and then stirred for an additional 30 min at room temperature. To this mixture were added saturated aqueous hydrogen carbonate (20

cm^3) and ethyl acetate (20 cm^3). The organic layer was separated, washed with saturated aqueous carbonate (4 × 20 cm^3) dried ($MgSO_4$) and evaporated under reduced pressure to afford a pale yellow solid. Recrystallization of this from diethyl ether–hexane (1:2) provided *p*-dinitrobenzene (57 mg, 95%) as a colourless crystalline solid. The characteristic spectral data are as follows. *p*-Dinitrobenzene, m.p. 172–174 °C; ν_{max}(KBr)/cm^{-1} 3118, 3090, 1559vs, 1347vs, 1320, 1108, 1012, 875, 841 and 711; $\delta_H(CDCl_3)$ 8.43 (4 H, s); δ_C 124.86. 2,5-Dimethyl-*p*-dinitrobenzene (92%), m.p. 143–144 °C; ν_{max}(KBr)/cm^{-1} 2954, 1543vs, 1349vs, 1102 and 849; $\delta_H(CDCl_3)$ 2.62 (6 H, s) and 7.92 (2 H, s); δ_C 19.58, 128.55, 132.42 and 150.73; *m/z* 196 (M^+). 2,6-Dimethyl-*p*-dinitrobenzene (93%); m.p. 92–94 °C; ν_{max}(KBr)/cm^{-1} 2974, 2933, 2878, 1545vs, 1463, 1347vs, 1272, 1074, 910 and 848; $\delta_H(CDCl_3)$ 2.34 (6 H, s) and 7.96 (2 H, s); δ_C 17.46, 124.01, 131.61, 147.55 and 154.88. 2-Isopropyl-5-methyl-*p*-dinitrobenzene (88%); m.p. 67–68 °C; ν_{max}(KBr)/cm^{-1} 2973, 1545vs, 1348vs, 1274, 1074 and 849; $\delta_H(CDCl_3)$ 1.31 (6 H, d), 2.61 (3 H, s), 3.36 (1 H, m), 7.65 (1 H, s) and 8.02 (1 H, s); δ_C 19.63, 23.32, 28.57, 124.20, 127.59, 132.34 and 141.59. 2,5-Diisopropyl-*p*-dinitrobenzene (93%), m.p. 113–115 °C; ν_{max}(KBr)/cm^{-1} 2974, 1544vs, 1347vs, 1274, 1075 and 849; $\delta_H(CDCl_3)$ 1.23 (12 H, d), 3.29 (2 H, m) and 7.66 (1 H, s); δ_C 23.27, 28.27, 123.56, 141.41 and 151.36. 2,5-Di-*tert*-butyl-*p*-dinitrobenzene (95%), m.p. 177–179 °C; ν_{max}(KBr)/cm^{-1} 2954, 1539vs, 1349vs, 1102 and 896; $\delta_H(CDCl_3)$ 1.39 (18 H, d) and 7.44 (2 H, s); δ_C 30.25, 35.57, 124.36, 140.90 and 151.43.

Stoichiometric Oxidation of Quinone Dioximes with Nitrogen Dioxide.—To a cooled (−10 °C) slurry of 2,5-di-*tert*-butyl-*p*-benzoquinone dioxime (100 mg, 0.4 mmol) in dichloromethane (30 cm^3) was added a pre-chilled solution of nitrogen dioxide in dichloromethane (0.2 mol dm^{-3}; 2 cm^3, 0.4 mmol) under an argon atmosphere. The suspension immediately turned greenish yellow. The mixture was stirred for an additional 30 min at room temperature to yield a clear yellow–green solution, removal of solvent under reduced pressure from which afforded a green residue. The crude product was dissolved in hexane and filtered through a short pad of silica gel with ethyl acetate–hexane (1:20) as eluent. Evaporation of the solvent under reduced pressure afforded 2,5-di-*tert*-butyl-*p*-dinitrosobenzene **6** (91 mg, 92% yield) as a bright green crystalline solid.

Catalytic Autoxidation of the Quinone Dioxime **6** *using Nitrosonium Tetrafluoroborate.*—In a typical procedure, a flask was charged with nitrosonium tetrafluoroborate (4.6 mg, 0.04 mmol) in the dry box. Dichloromethane (10 cm^3) was added under an oxygen atmosphere to the flask, to which an O_2-filled balloon was attached to the side arm. To the above mixture was added 2,5-di-*tert*-butyl-*p*-benzoquinone dioxime (100 mg, 0.4 mmol) and the reaction mixture stirred overnight at room temperature to yield a yellow–green solution. After removal of solvent under reduced pressure from the solution, dichloromethane (10 cm^3) and saturated aqueous sodium hydrogen carbonate (20 cm^3) were added to the residue. The organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure to afford a green solid, further purification of which by column chromatography on silica gel with ethyl acetate–hexane (1:20) provided 2,5-di-*tert*-butyl-*p*-dinitrosobenzene (95 mg, 96%) as a green crystalline solid.

Stoichiometric Reaction of the Quinone Dioxime **6** *with Nitrosonium Tetrafluoroborate.*—Typically, nitrosonium tetrafluoroborate (84 mg, 0.8 mmol) was charged in a Schlenk flask in the glove box. Dry acetonitrile (20 cm^3) and 2,5-di-*tert*-butyl-*p*-benzoquinone dioxime **6** (100 mg, 0.4 mmol) were added to the flask and the mixture was stirred under an argon atmosphere. The mixture immediately changed to yellowish green and was stirred for an additional 5 min. Spectral analyses (UV and IR) of the head gas indicated the presence of only nitric oxide. The solvent was removed under reduced pressure to give a brown solid. The crude product was dissolved in dichloromethane (20 cm^3) and the solution washed with aqueous sodium hydrogen carbonate (2 × 20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to afford the dinitrosobenzene **6** as a green crystalline solid (94 mg, 95%).

Acknowledgements

We thank the National Science Foundation, R. A. Welch Foundation, and the Texas Advanced Research Project for financial assistance.

References

1 (*a*) N. P. Tikhonova, L. V. Ginzburg and A. A. Dontsov, *Kauch. Rezina.*, 1987, **3**, 13; (*b*) P. Ruggli, *Helv. Chim. Acta*, 1938, **21**, 711.
2 (*a*) R. Hoffmann, R. Gleiter and F. B. Mallory, *J. Am. Chem. Soc.*, 1970, **92**, 1460; (*b*) S. Marriott, R. D. Topsom and B. G. Gowenlock, *J. Phys. Chem.*, 1990, **94**, 5220; (*c*) G. Butt and R. D. Topsom, *J. Mol. Struct. (Theochem)*, 1988, **164**, 399; (*d*) A. R. Katritzky, H. J. Keogh, S. Ohlenrott and R. D. Topsom, *J. Am. Chem. Soc.*, 1970, **92**, 6855; (*e*) M. D. Lumsden, G. Wu, R. E. Wasglishen and R. D. Curtis, *J. Am. Chem. Soc.*, 1993, **115**, 2825.
3 C. N. R. Rao and K. R. Bhaskar, *The Chemistry of The Nitro and Nitroso Groups*, ed. H. Feuer, Interscience Publishers, 1969, Part 1, p. 137.
4 K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, 1956, **78**, 1113.
5 (*a*) J. H. Boyer, U. Toggweiller and G. A. Stoner, *J. Am. Chem. Soc.*, 1957, **79**, 1748; also see references cited therein; (*b*) H. A. Pinner, *Ber.*, 1900, 3557.
6 Y. S. Khishchenko, M. A. Makarov, G. A. Gareev, N. A. Cherkashina and G. S. Koptina, *Zh. Prikl. Khim.*, 1969, **42**, 2384 (*Chem. Abstr.*, 1970, **72**, 31347).
7 O. A. Ermakov and Y. F. Komkova, *Zh. Org. Khim.*, 1984, **20**, 2252.
8 T. Zincke and P. Schwarz, *Ann.*, 1899, **40**, 307.
9 J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner and F. Sahhar, *J. Am. Chem. Soc.*, 1955, **77**, 5688.
10 R. Rathore, E. Bosch and J. K. Kochi, *Tetrahedron Lett.*, 1994, **35**, 1335; see also E. Bosch, R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1994, **59**, 2529.
11 G. Kokkinidis and G. Papanastasiou, *J. Electroanal. Chem.*, 1988, **257**, 239.
12 F. F. Marmo, *J. Opt. Soc. Am.*, 1953, **42**, 1186. Compare E. Bosch, *et al.* in reference 10.
13 W. G. Fately, H. A. Bent and B. Crawford, Jr., *J. Chem. Phys.*, 1959, **31**, 204.
14 T. C. Hall, Jr. and F. E. Blacet, *J. Chem. Phys.*, 1952, **20**, 1745.
15 J. A. Smith, *J. Am. Chem. Soc.*, 1943, **65**, 74.
16 E. Bosch and J. K. Kochi, *J. Org. Chem.*, in press.
17 E. Steckhan, *Organic Electrochemistry*, 3rd edn., ed. H. Lund and M. M. Baizer, Marcel Dekker Inc., p. 594.
18 (*a*) O. Hammerich and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1982, **36**, 63; (*b*) V. D. Parker, *Electrochimica Acta*, 1973, **18**, 519.
19 E. Bosch and J. K. Kochi, *Res. Chem. Intermed.*, 1993, **16**, 811.
20 (*a*) W. R. Forsythe and W. F. Giauque, *J. Am. Chem. Soc.*, 1942, **64**, 48; (*b*) A. Boughriet, J. C. Fischer and M. Wartel, *Bull. Soc. Chim. Fr.*, 1985, I-8.
21 I. R. Beattie and S. W. Bell, *J. Chem. Soc.*, 1957, 1681.
22 K. Y. Lee, D. J. Kuchynka and J. K. Kochi, *Inorg. Chem.*, 1990, **29**, 4196.
23 (*a*) S. Sorriso, *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*, ed. S. Patai, John Wiley, 1982, p. 43; (*b*) J. H. Boyer, *The Chemistry of The Nitro and Nitroso Groups*, ed. H. Feuer, Interscience Publishers, 1969, Part 1, ch. 5.
24 (*a*) D. A. Dieterich, I. C. Paul and D. Y. Curtin, *Chem. Commun.*, 1970, 1710; also see references cited therein; (*b*) C. Darwin, D. C. Hodgkin, *Nature*, 1950, 827; (*c*) C. K. Prout, T. S. Cameron, R. M. A. Dunn, O. J. R. Hodder and D. Viterbo, *Acta Cryst., Sect. B*, 1971, **27**, 1310; (*d*) C. P. Fenimore, *J. Am. Chem. Soc.*, 1950, **72**, 3226; (*e*) P. G. Germain, P. Piret and M. V. Meerssche, *Acta Cryst.*, 1963, **16**, 109; (*f*) F. P. Boer and J. W. Turley, *J. Am. Chem. Soc.*, 1969, **91**, 1371.
25 P. Ruggli and G. Bartusch, *Helv. Chim. Acta*, 1944, **27**, 1371.

26 (*a*) C. C. Addison, *Chemistry in Liquid Dinitrogen Tetroxide*, Vieweg, Braunschweig, 1967, (*b*) C. C. Addison and D. Sutton, *Progr. Inorg. Chem.*, 1967, **8**, 195.
27 V. A. Bogolyubskii, *Zh. Obshch. Khim.*, 1962, **32**, 869.
28 (*a*) E. Kremers, N. Wakeman and R. M. Hixon, *Org. Synth.*, Coll. Vol. I, 1941, 511; (*b*) R. K. Norris and S. Sternhell, *Aust. J. Chem.*, 1966, **19**, 841.
29 P. Jacob, III, P. S. Callery, A. T. Shulgin and N. Castagnol, Jr., *J. Org. Chem.*, 1976, **41**, 3627.

Paper 4/02540G
Received 28*th April* 1994
Accepted 20*th June* 1994