

## Oxidative Dealkylation of Hydroquinone Ethers with Nitrogen Dioxide in the Convenient Preparation of Quinones

Rajendra Rathore, Eric Bosch and Jay K. Kochi  
Chemistry Department, University of Houston, Houston, TX 77204-5641, USA

Various hydroquinone dialkyl ethers ( $R_2Q$ ) are effectively converted by nitrogen dioxide into the corresponding quinone (Q) and alkyl nitrite (RONO) in dichloromethane at room temperature or below. The preparative procedure for the isolation of crystalline quinones in quantitative yield merely involves the convenient removal of the low boiling solvent *in vacuo*. Isotopic labelling studies demonstrate that the oxidative dealkylation proceeds *via* alkoxy scission of the labile cation radical ( $R_2Q^{\cdot+}$ ) formed *via* the oxidation of the hydroquinone ether by nitrogen dioxide (as the disproportionated ion pair  $NO^+NO_3^-$ ). The electron-transfer mechanism is confirmed by the spectral observation of  $R_2Q^{\cdot+}$  (identified by the isolation of the crystalline salt  $R_2Q^{\cdot+}SbCl_6^-$ ) and its rapid conversion into quinone and alkyl nitrite by combination with nitrate ( $NO_3^-$ ) and nitric oxide (NO).

Oxidative dealkylation (especially demethylation) of hydroquinone dialkyl ethers is relevant to both synthetic and biological chemistry.<sup>1-3</sup> Corey and Link<sup>4</sup> have recently applied this transformation to the synthesis of optically active alcohols ( $R^*OH$ ) *via* the treatment of the corresponding 1-alkoxy-4-methoxybenzenes with an excess of ceric ammonium nitrate (CAN) in aqueous dimethylformamide. It is noteworthy that the liberation of the chiral alcohol proceeded with retention of configuration (*i.e.*,  $R^*OH$ ). In addition to cerium(IV) nitrate,<sup>5</sup> the successful use of silver(II) oxide<sup>6</sup> and concentrated nitric acid<sup>7</sup> has been reported for the facile demethylation of hydroquinone ethers. However, all of these preparative methods require aqueous and acidic conditions that may be deleterious to bio-quinones, especially those with acid-sensitive functionalities. In the course of our studies of nitrogen dioxide,<sup>8</sup> we found that substituted 1,4-dialkoxybenzenes were quantitatively converted into the corresponding *p*-benzoquinones in non-polar solvents under essentially neutral (non-acidic) conditions.<sup>9</sup> Accordingly in this report, we report a convenient methodology for the preparative conversion of such dialkoxybenzenes into quinones under unusually mild conditions. We also describe the complex (redox) chemistry involving a multitude of nitrogen oxides that underlies this seemingly straightforward transformation.

### Results

**Preparative Conversions of Substituted 1,4-Dialkoxybenzenes into Quinones with Nitrogen Dioxide.**—When a solution of durohydroquinone dimethyl ether in dichloromethane at  $-78^\circ C$  was treated under an argon atmosphere with 2 equiv. of nitrogen dioxide, the solution turned dark orange (red) immediately. On standing, the orange solution was slowly transformed into a clear pale yellow solution, but the bleaching occurred very rapidly upon warming to room temperature. Spectral analysis of the head gas revealed the characteristic (UV and IR) absorptions of methyl nitrite with resolved vibrational

fine structure at  $\lambda$  301, 306, 310, 318, 329, 340, 351, 365 and 389 nm,<sup>10</sup> and  $\nu$  1611, 1621, 1638, 1668 and 1687  $cm^{-1}$ ,<sup>11</sup> respectively. Removal of the solvent (together with the gaseous methyl nitrite) *in vacuo* led to a quantitative yield of crystalline duroquinone, eqn. (1), which was essentially free of organic impurities (< 1%) by  $^1H$  NMR and GC-MS analysis.

In order to establish the generality of quinone synthesis according to eqn. (1), a variety of hydroquinone ethers listed in

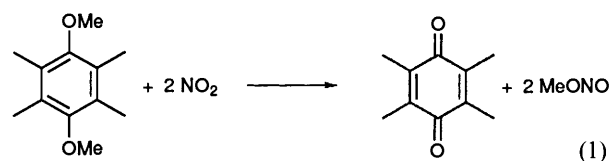
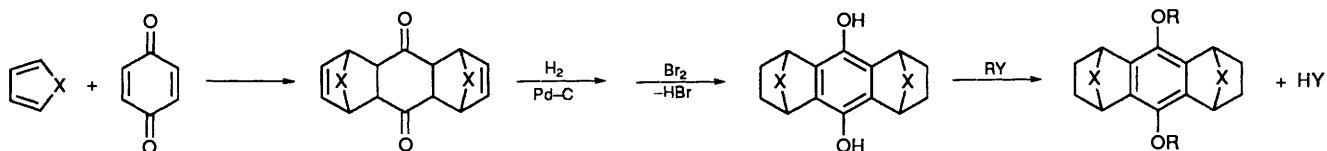


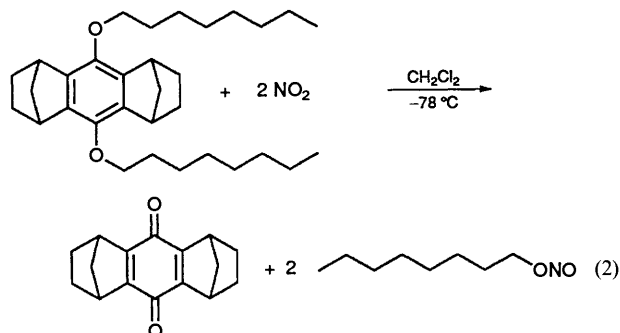
Table 1 were prepared by the Diels-Alder condensation of *p*-benzoquinone with different dienes followed by bromine aromatization<sup>12</sup> and alkylation,<sup>13</sup> *i.e.*, Scheme 1, where  $-X-$  =  $-CH_2-$ ,  $-CH_2CH_2-$  and  $-H,H-$ , and R = methyl, ethyl, isopropyl and *n*-octyl. In each case, the oxidative dealkylation of the hydroquinone ethers with nitrogen dioxide in dichloromethane under an argon atmosphere led to quantitative yields of the corresponding quinones, which were readily isolated in pure form simply by the removal of the solvent (and RONO) *in vacuo*.

Optimum conditions for  $NO_2$  usage were examined by treating the dimethyl ether **1a** with various molar ratios of  $NO_2$ . For example, when an equimolar amount of  $NO_2$  was added to 1 equiv. of **1a** in dichloromethane under an argon atmosphere, only 0.5 equiv. of quinone **1Q** was isolated, and the remainder (0.5 equiv.) of the dimethyl ether was recovered intact. With higher molar ratios of  $[NO_2]:[1a] = 3:1$  and  $4:1$ , complete conversion into quinone occurred, and the excess nitrogen dioxide was clearly identified by its characteristic IR spectrum [ $\nu_{NO} = 1604$  and  $1621$   $cm^{-1}$ ].<sup>14</sup> Owing to the difficulty of precisely assessing the amount of the gaseous methyl nitrite

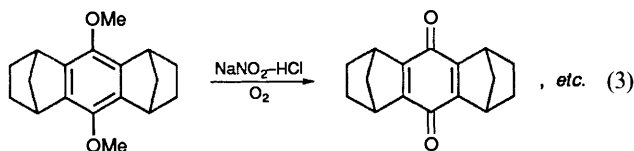


Scheme 1

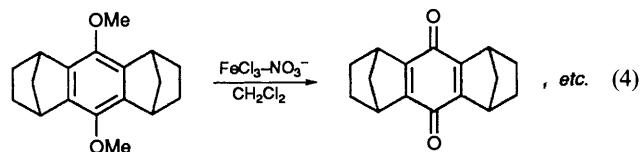
produced during the dealkylation, we turned to the less volatile di-*n*-octyl ether analogue **1d**. When **1d** was treated with 2 equiv. of NO<sub>2</sub> in dichloromethane as detailed above, a quantitative yield of quinone **1Q** (1 equiv.) was obtained together with 2 equiv. of *n*-octyl nitrite in eqn. (2). The latter was quantitatively characterized by comparison of the <sup>1</sup>H NMR spectrum with that of an authentic sample,<sup>15</sup> using the internal standard method.



The oxidative dealkylation of hydroquinone ethers could also be carried out with other, more convenient sources of nitrogen dioxide, such as an inexpensive mixture of air, sodium nitrite and hydrochloric acid. For example, a heterogeneous mixture of sodium nitrite (2 equiv.) and dimethyl ether **1a** in dichloromethane under a dioxygen atmosphere was cooled to -10 °C in an ice-acetone bath. The mixture was stirred (magnetically), while excess hydrochloric acid was added with the aid of an all-glass hypodermic syringe. After 1 h, anhydrous magnesium sulfate was added, the mixture filtered, and the pale yellow solution evaporated *in vacuo* to afford quinone **1Q** in quantitative yield, eqn. (3). [In this procedure, note that nitrous acid produced in the neutralization of sodium nitrite decomposed readily to dinitrogen trioxide,<sup>16</sup> which was rapidly oxidized *in situ* to nitrogen dioxide by dioxygen.<sup>17</sup>]

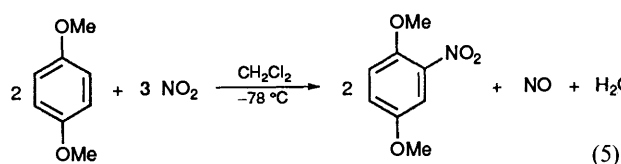


High yields of quinone were also obtained by an alternative anaerobic procedure, in which the oxidant ferric chloride (2 mmol) was added to a solution of the dimethyl ether **1a** (1 mmol) and a soluble nitrate salt (2 mmol)<sup>18</sup> in dichloromethane at -10 °C. The transient bright orange mixture turned, within 10 min, into a clear, pale yellow solution from which the crystalline quinone **1Q** was isolated in 98% yield, eqn. (4).

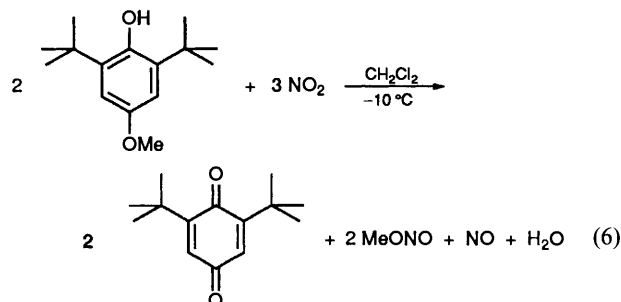


Oxidative dealkylations with nitrogen oxides were best suited to fully substituted hydroquinone ethers, such as those listed in Table 1. While the tetramethyl and tetraethyl hydroquinone ethers **10** and **9** were quantitatively dealkylated, as described above, the trimethyl hydroquinone homologue under the same conditions gave trimethyl-*p*-benzoquinone in only 80% yield, together with a variety of by-products including the nitration product 2,5-dimethoxy-(3,4,6-trimethyl)nitrobenzene. It is thus noteworthy that nitration was the sole course of reaction when the parent hydroquinone ether was exposed to nitrogen dioxide. Thus the treatment of 1,4-dimethoxybenzene with NO<sub>2</sub> at -78 °C in dichloromethane under an argon atmosphere

yielded 2-nitro-1,4-dimethoxybenzene in quantitative yield according to the stoichiometry in eqn. (5).<sup>19</sup> The formation of nitric oxide (and the absence of methyl nitrite<sup>10,11</sup>) in eqn. (5)



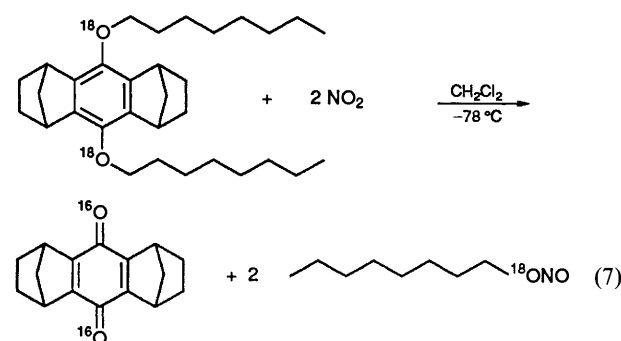
was established from the IR analysis of the head gas ( $\nu_{\text{NO}} = 1876 \text{ cm}^{-1}$ <sup>20</sup>). By comparison, the sterically hindered hydroquinone monomethyl ether yielded a mixture of nitric oxide and methyl nitrite, together with a quantitative yield of 2,6-di-*tert*-butyl-1,4-benzoquinone according to the stoichiometry in eqn. (6). [It should be noted that the oxidative cleavage



of a pair of alkyl groups in hydroquinone diethers requires 2 equiv. of NO<sub>2</sub> to produce 2 equiv. of alkyl nitrite, whereas the conversion of both hydroxy groups in hydroquinone into benzoquinone requires 1 equiv. of NO<sub>2</sub> to produce 1 equiv. of NO and H<sub>2</sub>O.<sup>9</sup>]

Other fully substituted hydroquinone ethers such as that (**12**) derived from the relatively electron-poor tetrachlorohydroquinone were immune to oxidative dealkylation with NO<sub>2</sub>. Moreover, the acetate derivatives of the hydroquinones such as **11** (see Table 1) were similarly unreactive under these reaction conditions.

*Oxidative Dealkylation of <sup>18</sup>O-Labelled Hydroquinone Ether.*—Regiospecificity in the oxidative dealkylation of hydroquinone ethers was examined with the <sup>18</sup>O-labelled dioctyl ether **1d** prepared *via* the isotopically enriched quinone **1Q** according to Jacob *et al.*<sup>5</sup> Treatment of the doubly <sup>18</sup>O-labelled ether with two equiv. of NO<sub>2</sub> at -78 °C in dichloromethane under an argon atmosphere yielded crystalline quinone **1Q** which was completely free of the isotopic <sup>18</sup>O label, as judged by the mass spectral comparison with an authentic sample. Instead the <sup>18</sup>O labels were present only in the octyl nitrite fraction,<sup>21</sup> as described in eqn. (7). This result clearly established the



oxidative dealkylation with NO<sub>2</sub> to proceed *via* the scission of both aromatic-alkoxy bonds of the hydroquinone ether.

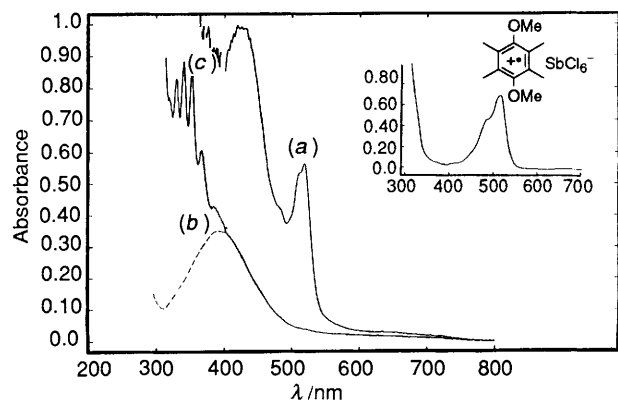
*Identification of Aromatic Cation Radicals as the Reactive Intermediate in Oxidative Dealkylation of Hydroquinone*

**Table 1** Oxidative dealkylation of hydroquinone ethers with nitrogen dioxide<sup>a</sup>

Substrate	Quinone <sup>b</sup>	Alkyl nitrite <sup>c</sup>	Substrate	Quinone <sup>b</sup>	Alkyl nitrite <sup>c</sup>
1		RONO	7		MeONO
1a	R = Me	MeONO	8		MeONO
1b	R = Et	EtONO	9		MeONO
1c	R = Pr <sup>i</sup>	Pr <sup>i</sup> ONO	10		MeONO
1d	R = <i>n</i> -Octyl	<i>n</i> -OctylONO	11		No reaction <sup>d</sup>
2		MeONO	12		No reaction <sup>d</sup>
3		MeONO	13		MeONO + NO
4		MeONO			
5		MeONO			
6		MeONO			

<sup>a</sup> Reactions were performed by mixing equal volumes of prechilled ( $-78^{\circ}\text{C}$ ) dichloromethane solutions of  $\text{NO}_2$  ( $0.2\text{ mol dm}^{-3}$ ) and dialkoxyarenes ( $0.1\text{ mol dm}^{-3}$ ). <sup>b</sup> Yields were quantitative (*i.e.*, free from impurities according to GC and NMR analysis). <sup>c</sup> Alkyl nitrites (except octyl nitrite) were not quantified. <sup>d</sup> See the text.

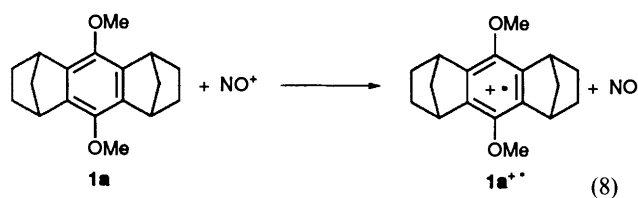
**Ethers.**—The oxidative dealkylation of hydroquinone ethers by the three different procedures described in eqns. (1)–(4), however disparate, all share in common an unmistakable orange colouration which was transient, the intensity and duration being dependent roughly on the speed of the dealkylation. Since these are the earmarks of a reactive intermediate,<sup>22</sup> we carefully monitored the absorption spectrum (see Fig. 1) immediately attendant upon the mixing of



**Fig. 1** Spectral changes attendant upon the treatment of  $0.01\text{ mol dm}^{-3}$  hydroquinone ether **1a** with  $0.2\text{ mol dm}^{-3}$  nitrogen dioxide at  $-78^{\circ}\text{C}$  in dichloromethane showing the formation of the cation radical [band (a)]. The final spectrum obtained after the solution was warmed to  $25^{\circ}\text{C}$  and recooled to  $-78^{\circ}\text{C}$  to show the formation of quinone IQ [band (b)] and methyl nitrite [band (c)]. Inset: the absorption spectrum of the radical cation  $\mathbf{1a}^{+\bullet}$  salt  $9.6 \times 10^{-5}\text{ mol dm}^{-3}$  [ $\mathbf{1a}^{+\bullet}\text{SbCl}_6^-$ ] in dichloromethane for comparison with band (a).

hydroquinone ether **1a** with nitrogen dioxide at  $-78^{\circ}\text{C}$ . The orange colour is shown in Fig. 1 to arise largely from a species with a distinctive absorption band (a) with  $\lambda_{\text{max}} = 518\text{ nm}$  (shoulder,  $486\text{ nm}$ ). Spectral band (a) was readily assigned to the cation radical ( $\mathbf{1a}^{+\bullet}$ ) of the hydroquinone ether by an independent synthesis with nitrosonium as the 1-electron oxidant,<sup>23</sup> eqn. (8). The same cation radical was prepared from antimony pentachloride<sup>24</sup> as a single crystal of [ $\mathbf{1a}^{+\bullet}\text{SbCl}_6^-$ ] suitable for X-ray crystallography (Fig. 2).<sup>25</sup> The absorption spectrum of the pure cation radical [ $\lambda_{\text{max}} = 518\text{ nm}$  ( $\epsilon$ ,  $7300\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ), shoulder  $486\text{ nm}$ ] is illustrated in the inset to Fig. 1 for spectral comparison with absorption band (a). With the passage of time, the intense visible absorption diminished, and the resultant pale yellow solution showed the characteristic absorption band (b) of the quinone IQ superimposed onto the vibrationally resolved absorption spectrum (c) of methyl nitrite.<sup>10</sup>

The coloured cation radical was an unmistakable (visible) feature in the oxidative dealkylation of most of the hydroquinone ethers listed in Table 1. Thus all the pentacyclic hydroquinone ethers **1–5** afforded (orange/red) cation radicals with  $\text{NO}^+$  [eqn. (8)] that were persistent in dichloromethane



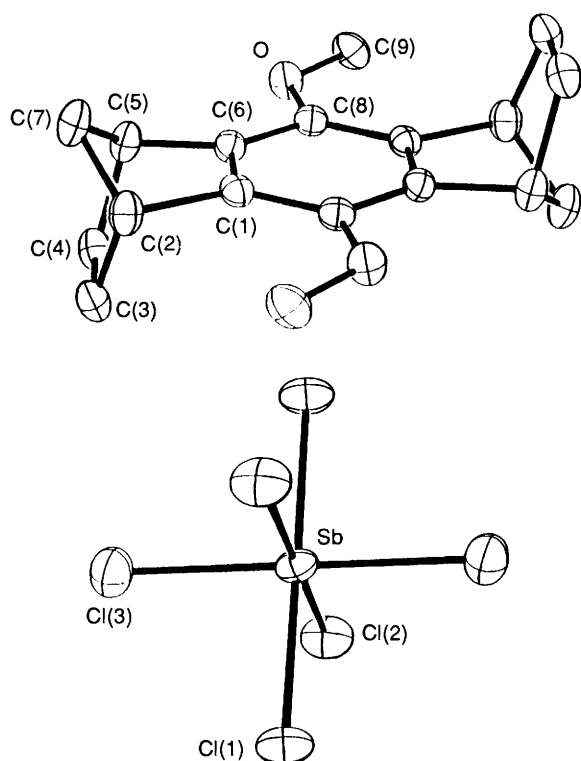
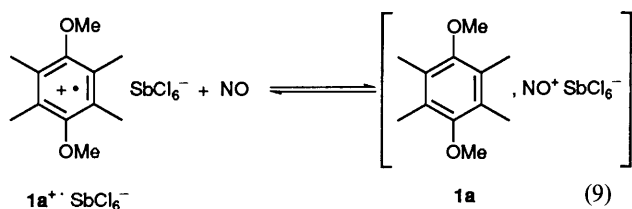


Fig. 2 ORTEP drawing of the radical cation salt  $[1a^+ SbCl_6^-]$  with the hydrogens omitted for clarity

solution. The tetracyclic and tricyclic analogues **6** and **7** were less so, and those (**8–10**) with simple alkyl substituents were quite transient. In accord with this trend, the degree to which the orange (red) colour could be temporally observed during oxidative dealkylation with nitrogen dioxide diminished monotonically on proceeding from **1** to **10**. Consequently, further mechanistic analysis of oxidative dealkylation required our direct examination of the radical cation of hydroquinone ethers with the various nitrogen oxides present under reaction conditions.

**Reactivity of Aromatic Cation Radicals toward Nitrogen Oxides.**—The crystalline radical cation salt  $[1a^+ SbCl_6^-]$  was chosen for study with the predominant nitrogen oxides  $NO_x = NO, NO_3^-$  and  $NO_2$ , as follows.

**Nitric oxide.** When a dichloromethane solution of the cation radical salt  $[1a^+ SbCl_6^-]$  was exposed to nitric oxide (gas) at  $25^\circ C$ , the orange colour diminished perceptibly. On cooling, the solution lightened progressively until the orange colour disappeared at  $-78^\circ C$ . Conversely, the colour intensified on warming the solution. The quantitative effects of this dramatic colour change (which was completely reversible over multiple cooling–warming cycles) are illustrated in Fig. 3.<sup>26</sup> The single isosbestic point confirmed the temperature-dependent electron transfer in eqn. (9).



**Nitrate.** When a solution of the nitrate salt<sup>18</sup>  $PPN^+ NO_3^-$  (1 equiv.) was added at  $0^\circ C$  to the equilibrated mixture of  $1a^+$  and  $NO$  in eqn. (9), the orange solution was immediately

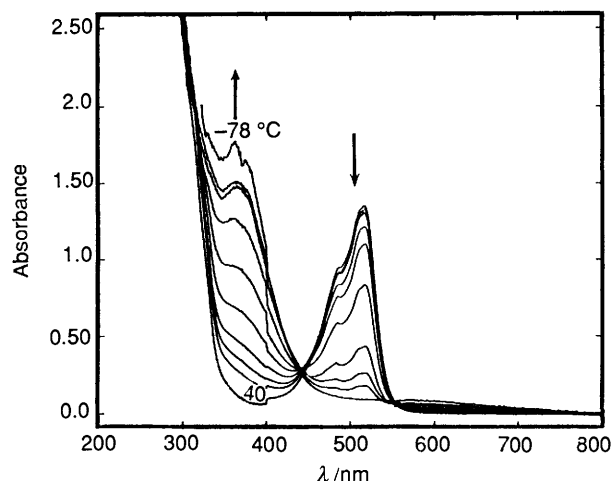
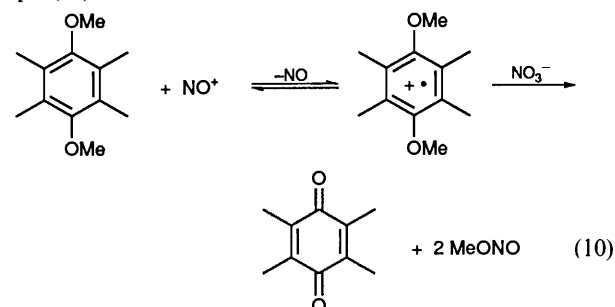
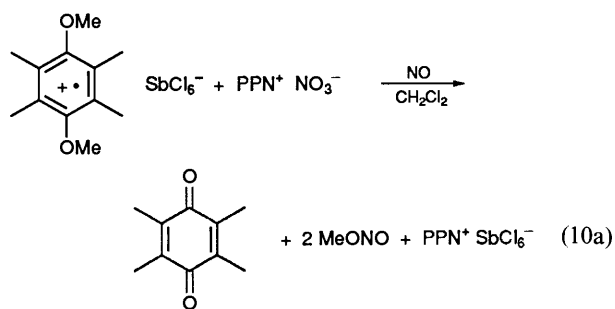


Fig. 3 Temperature-dependent spectral change accompanying the exposure of  $2 \times 10^{-4} \text{ mol dm}^{-3} [1a^+ SbCl_6^-]$  to nitric oxide in dichloromethane from  $+40^\circ$  to  $-78^\circ C$  (incrementally)

bleached. Spectral analysis of the pale yellow solution revealed the presence of methyl nitrite and quinone **1Q**, which was isolated in quantitative yield according to the stoichiometry in eqn. (10). The same results were obtained when a solution of

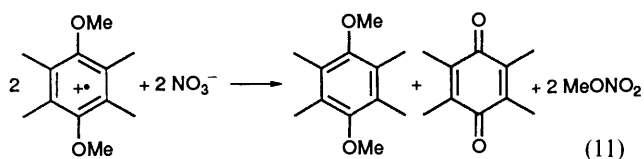


$PPN^+ NO_3^-$  (1 mmol) in dichloromethane was added to an  $NO$ -saturated solution of the radical cation salt  $[1a^+ SbCl_6^-]$  (1 mmol) in dichloromethane at  $-78^\circ C$  under an argon atmosphere. Following the decolourisation of the orange solution, only quinone **1Q** (1 mmol) was isolated together with methyl nitrite, eqn. (10a). In a control experiment, purified  $NO$



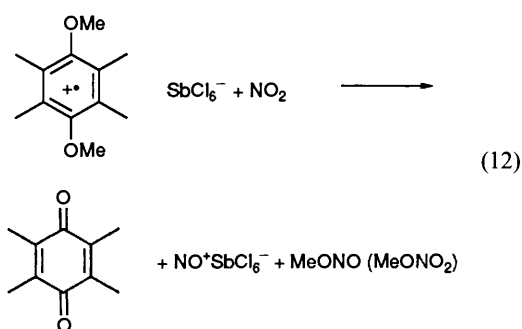
was bubbled through a colourless solution of the hydroquinone ether **1a** and  $PPN^+ NO_3^-$  in dichloromethane at  $-78^\circ C$  with no apparent change. The solution was stirred for several days at  $25^\circ C$ , after which the hydroquinone ether was recovered quantitatively after the solvent and nitric oxide had been removed *in vacuo*, followed by extraction of the salt.

In order to confirm the direct involvement of the radical cation  $1a^+$  with nitrate in eqns. (10) and (10a), the orange salt  $[1a^+ SbCl_6^-]$  was treated directly with an equimolar amount of  $PPN^+ NO_3^-$  in dichloromethane solution at  $-78^\circ C$  under an argon atmosphere. Following the immediate bleaching of the orange solution, an equimolar mixture of quinone (**1Q**) and hydroquinone ether (**1a**) was isolated according to the stoichiometry in eqn. (11). The identity of the  $NO_x$ -containing



product as methyl nitrite was confirmed by its characteristic IR bands at 3056, 2987, 2306, 1638, 1423, 1288, 1264, 1157, 995, 897 and 862  $\text{cm}^{-1}$  and  $^1\text{H}/^{13}\text{C}$  NMR spectra ( $\delta$  4.03/59.61).<sup>27</sup> It is noteworthy that the methyl nitrite formed in eqns. (9) and (10) was absent.

**Nitrogen dioxide.** The addition of nitrogen dioxide (3 equiv.) to a dichloromethane solution containing 1 equiv. of the radical cation salt [ $\mathbf{1a}^{\bullet+}\text{SbCl}_6^-$ ] at  $-78^\circ\text{C}$  led to a steady decrease in the absorbance of  $\mathbf{1a}^{\bullet+}$  ( $\lambda_{\text{max}} = 516 \text{ nm}$ ).<sup>28</sup> On standing at room temperature, the clear, yellow solution deposited a white precipitate of  $\text{NO}^+\text{SbCl}_6^-$ . The yellow solution upon GC-MS analysis indicated the presence of quinone  $\mathbf{1Q}$  in 80% yield,<sup>29</sup> together with an equimolar mixture of methyl nitrite and methyl nitrate, eqn. (12). The yield of quinone  $\mathbf{1Q}$  was

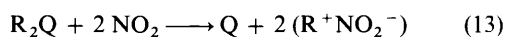


diminished when excess nitrogen dioxide was employed. [Note that methyl nitrite was not converted by nitrogen dioxide into methyl nitrate under the reaction conditions.]

## Discussion

Treatment of the hydroquinone ethers in Table 1 with 2 equiv. of nitrogen dioxide in dichloromethane at room temperature (or below) readily leads to the corresponding 1,4-quinones (and alkyl nitrite) according to the prototypical stoichiometry described in eqns. (1) and (2). The mild (non-acidic) reaction conditions employed, coupled with the trivial work-up procedure for the ready isolation of pure quinones in essentially quantitative yields, establish this to be the method of choice for the oxidative dealkylation of fully substituted hydroquinone ethers. Furthermore, the alternative use of sodium nitrite-hydrochloric acid in air [eqn. (3)] provides a cheap alternative to nitrogen dioxide without a noticeable sacrifice in efficiency.

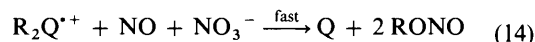
Formally, the oxidative dealkylation of hydroquinone dialkyl ethers ( $\text{R}_2\text{Q}$ ) to quinones ( $\text{Q}$ ) with nitrogen dioxide involves the overall removal of two electrons and two alkyl cations (in the form of alkyl nitrite), eqn. (13). However, the isotopic labelling



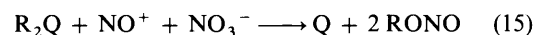
studies [eqn. (7)] demonstrate that the alkyl-oxygen bond remains intact since the  $^{18}\text{O}$  label resides exclusively in the alkyl nitrite. In this regard, the oxidative dealkylation with nitrogen dioxide is akin to those observed earlier with ceric ammonium nitrate<sup>5</sup> and silver(II) oxide.<sup>6</sup> Therefore, any mechanistic formulation of oxidative dealkylation must be reconciled with the alkyl loss from  $\text{R}_2\text{Q}$  *via* the scission of the alkoxy (and not the alkyl) bond. Such regioselectivity is counter to the usual

electrophilic process—the conventional acid-catalysed hydrolysis of aralkyl ethers proceeding exclusively *via* alkyl-oxygen and not aryl-oxygen cleavage.<sup>30</sup>

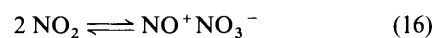
The spectral observation of the radical cation of hydroquinone ethers ( $\text{R}_2\text{Q}^{\bullet+}$ ) as a transient intermediate (Fig. 1), provides the key to understanding how the alkoxy bonds are cleaved in hydroquinone dialkyl ethers. Thus the independent treatment of the radical cation with a mixture of nitric oxide and nitrate in eqn. (10) confirms its rapid dealkylation to follow the prototypical stoichiometry in eqns. (1) and (2), *i.e.*, eqn. (14).



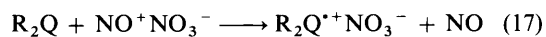
Since the nitric oxide [that is required for eqn. (14)] is formed directly from  $\text{R}_2\text{Q}$  *via* the electron-transfer equilibrium outlined in eqn. (9) [and (10)], it follows that a mixture of nitrosonium and nitrate will also effect oxidative dealkylation of hydroquinone ethers, eqn. (15). Such a cation-anion pair is known to



derive directly from the reversible disproportionation of nitrogen dioxide,<sup>31</sup> eqn. (16).



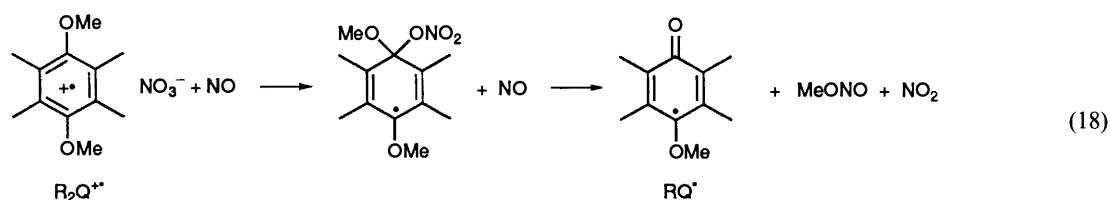
In other words, we identify the activation process for oxidative dealkylation of  $\text{R}_2\text{Q}$  with nitrogen dioxide to derive from electron transfer *via* the disproportionated ion pair [ $\text{NO}^+\text{NO}_3^-$ ] in eqn. (16). Such a formulation depends on the ability of the aromatic ether to undergo one-electron transfer to the nitrosonium moiety,<sup>23,32</sup> eqn. (17).



The electron-donor properties of the hydroquinone ethers in Table 1 decrease progressively on proceeding from  $\mathbf{1a}$  ( $E_{\text{ox}}^0 = 1.12 \text{ vs. SCE}$ ) to  $\mathbf{10}$  ( $E_{\text{ox}}^0 = 1.57$ ).<sup>25</sup> Based on the reduction potential for nitrosonium of  $E_{\text{red}}^0 = 1.50 \text{ vs. SCE}$  in dichloromethane solution,<sup>33</sup> the free-energy changes for electron transfer<sup>34</sup> in eqn. (17) are sufficient to promote oxidative dealkylation with nitrogen dioxide, certainly at rates consistent with the results in Table 1. It is noteworthy that the acetate analogue  $\mathbf{11}$  with the more positive oxidation potential of  $E_{\text{ox}}^0 = 1.86 \text{ vs. SCE}$ <sup>25</sup> was not subject to oxidative deacetoxylation. Likewise, four chlorine substituents reduce the donor strength of the hydrochloranil ether  $\mathbf{12}$  ( $E_{\text{ox}}^0 > 2 \text{ V}$ ) sufficiently to inhibit its oxidative dealkylation with nitrogen dioxide.

The facile loss of the alkoxy group from the cation radical in a subsequent step is shown by its rapid quenching by nitrate in eqn. (11)—most probably *via* the collapse of the ion pair in eqn. (17) at the *ipso* position,<sup>35</sup> eqn. (18). The loss of the second alkoxy group from the intermediate radical ( $\text{RQ}^{\bullet}$ ) in eqn. (18) can proceed *via* an analogous series of fast homolytic reactions involving oxidation, ion-pair collapse and elimination, *e.g.*, eqn. (19).

The extensive series of one-electron transformations outlined in eqns. (18) and (19) that follow the initial electron transfer [eqn. (17)] represent the bare minimum to account for the complex (redox) stoichiometry in eqns. (1) and (2). Since other combinations of paramagnetic species are possible, such as eqn. (20), we are unable at this juncture to delineate the mechanism of  $\text{NO}_2$ -induced oxidative dealkylation more precisely without undue speculation.<sup>37</sup> Nonetheless, the electron-transfer mechanism presented in this study does serve as a distinguishing feature in the regiospecific alkoxy (bond) cleavage of hydroquinone alkyl ethers. In this regard, it also provides the basis



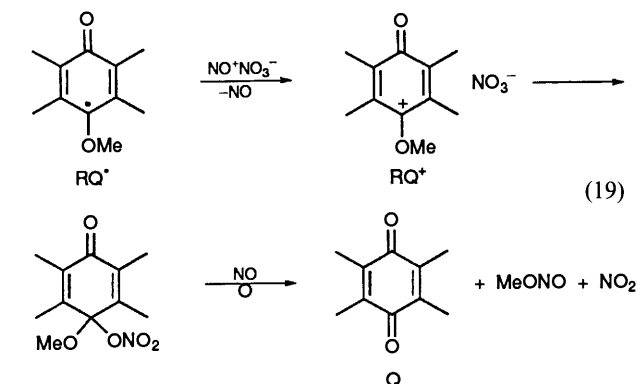
### Hydroquinone Dialkyl Ethers

**Preparation of 9,10-Dioctyloxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene 1d.**—The hydroquinone **1**<sup>12</sup> (4.8 g, 20 mmol) was added under an argon atmosphere to a solution of sodium ethoxide [freshly prepared by reacting sodium metal (1.38 g, 60 mmol) with ethanol at room temperature] in ethanol (50 cm<sup>3</sup>). The mixture was stirred for 20 min and octyl bromide (9.65 g, 50 mmol) was then added all at once and the mixture refluxed for 12 h. The reaction mixture was filtered (to remove precipitated sodium bromide) and diluted with water (100 cm<sup>3</sup>). The crystalline dioctyl derivative **1d** thus obtained was filtered and washed with water. Recrystallization from dichloromethane–ethanol mixture afforded pure **1d** (8.0 g, 86%), m.p. 57–59 °C;  $\delta_H$  0.88 (6 H, t, *J* 6.6), 1.15 (4 H, sym m), 1.25–1.88 (36 H, m), 3.49 (4 H, s) and 3.91 (4 H, ABM<sub>2</sub> system,  $\Delta\nu_{AB}$  19.2, *J*<sub>AB</sub> 9.37, *J*<sub>AM</sub> 6.59 and *J*<sub>BM</sub> 6.59);  $\delta_C$  14.09, 22.65, 26.13, 26.99, 29.30, 29.44, 30.36, 31.84, 40.72, 48.88, 73.88, 137.77 and 142.54; *m/z* 466 (M<sup>+</sup>).

**Preparation of 9,10-Dimethoxy-1,2,3,4,5,6,7,8-octahydroanthracene 8.**—Octahydro-9,10-hydroanthraquinone<sup>12</sup> (5.45 g, 25 mmol) was suspended in dioxane (50 cm<sup>3</sup>) in a 250 cm<sup>3</sup> flask under an argon atmosphere. A solution of potassium hydroxide (5.6 g, 100 mmol) in water (100 cm<sup>3</sup>) was added slowly to the reaction flask under a strong flow of argon. The mixture was stirred for 10 min and then dimethyl sulfate (12.6 g, 100 mmol) was added dropwise over 1 h. After the addition was complete, the mixture was refluxed for 3 h and cooled to room temperature. The mixture was then diluted with water (100 cm<sup>3</sup>) and extracted with dichloromethane (3 × 100 cm<sup>3</sup>). The organic layer was dried, filtered and the solvent removed *in vacuo*. A light brown crystalline residue was obtained and recrystallized from dichloromethane ethanol mixture to yield colourless plates (5 g, 82%); m.p. 59–61 °C;  $\delta_H$  1.70 (8 H, br s), 2.68 (8 H, br s) and 3.64 (6 H, d, *J* 1.5);  $\delta_C$  22.55, 23.43, 59.15, 128.22 and 151.90; *m/z* 246 (M<sup>+</sup>).

**Preparation of Dimethoxydurene 10.**—A yellow solution of duroquinone (4.1 g, 25 mmol) in hot glacial acetic acid (100 cm<sup>3</sup>) was heated to boiling and zinc dust (10 g) added in small portions. The colourless solution thus obtained was quickly filtered (the zinc dust residue washed with more acetic acid) and cooled in an ice bath. Crystalline durohydroquinone<sup>43</sup> was filtered off and dried *in vacuo* (3.86 g, 93%). Dimethoxydurene **10** was prepared by methylation of durohydroquinone (3.32 g, 20 mmol) using potassium hydroxide (4.5 g, 80 mmol) and dimethyl sulfate (10 g, 80 mmol) in dioxane–water, similar to the procedure described above (2.87 g, 74%); m.p. 109–110 °C;  $\delta_H$  2.18 (12 H, d, *J* 2.7) and 3.64 (6 H, d, *J* 2.1);  $\delta_C$  12.58, 60.14, 127.60 and 152.71; *m/z* 194 (M<sup>+</sup>).

**Preparation of Tetrachloro-1,4-dimethoxybenzene 12.**—A mixture of a solution of chloranil (6.15 g, 25 mmol) in ether (100 cm<sup>3</sup>) and sodium hydrogensulfite (12 g) in water (50 cm<sup>3</sup>) was heated with swirling.<sup>44</sup> The solution first became brown and then pale yellow within a few minutes. After separation of the aqueous layer, the ether layer was evaporated to yield hydrochloranil (5.5 g, 87%). The hydrochloranil (5 g, 20 mmol) was

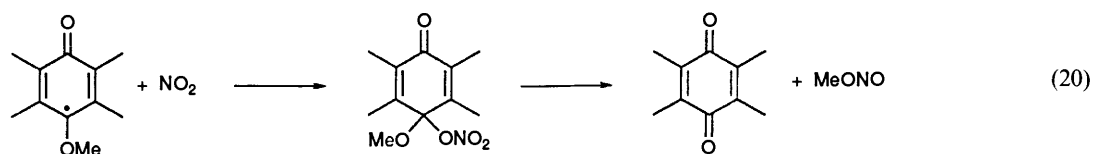


for the further mechanistic analysis of the related oxidative dealkylations with ceric ammonium nitrate<sup>5</sup> and silver(II) oxide,<sup>6</sup> which are otherwise also known to be one-electron oxidants.<sup>38,39</sup>

### Experimental

**Materials.**—Nitrosonium tetrafluoroborate (NO<sup>+</sup>BF<sub>4</sub><sup>-</sup>) (Pfaltz and Bauer) was stored in a Vacuum Atmosphere HE-493 dry box free from traces of oxygen, moisture, and solvent vapours. Nitrogen dioxide (Aldrich) was purified according to Addison.<sup>41,42</sup> Sodium nitrite (Aldrich) was used without further purification. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of conc. sulfuric acid (ca. 20% by volume) until the acid layer remained clear. After separation, it was washed successively with water, aqueous sodium hydrogen carbonate, water, and aqueous sodium chloride. Dichloromethane was dried over anhydrous calcium chloride, and distilled twice from P<sub>2</sub>O<sub>5</sub> under an argon atmosphere. It was stored in a Schlenk tube equipped with a Teflon valve fitted with Viton O-rings. Dialkyl ethers were prepared by alkylation of readily available hydroquinones<sup>12</sup> using standard procedures.<sup>13</sup> The properties and spectral data of the various dialkyl ethers **1a–c**, **2–7** and **9** will be presented elsewhere. 4-Methoxy-2,6-di-*tert*-butylphenol **13** and trimethyl-1,4-hydroquinone (Aldrich) were purified by repeated recrystallization from ethanol.

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



methylated as above to yield **12** (4.5 g, 81.5%), m.p. 158–160 °C;  $\delta_{\text{H}}$  3.87 (6 H, s);  $\delta_{\text{C}}$  60.78, 127.53 and 150.43;  $m/z$  176 ( $\text{M}^+$ ).

**Preparation of Trimethyl-1,4-dimethoxybenzene.**—Trimethyl-1,4-hydroquinone (3.8 g, 25 mmol) was methylated, as described for **8**, to yield trimethyl-1,4-dimethoxybenzene (3.6 g, 80%), m.p. 37–38 °C;  $\delta_{\text{H}}$  2.11 (3 H, s), 2.20 (3 H, s), 2.28 (3 H, s), 3.65 (3 H, d,  $J$  1.2), 3.77 (3 H, d,  $J$  1.5) and 6.53 (1 H, s);  $\delta_{\text{C}}$  11.84, 12.61, 16.27, 55.76, 60.11, 110.26, 127.66, 130.57, 150.49 and 153.32;  $m/z$  180 ( $\text{M}^+$ ).

**Preparation of 9,10-Diacetoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene 11.**—Acetyl chloride (ca. 5 cm<sup>3</sup>) was added dropwise to crystalline hydroquinone **1** (2.42 g, 10 mmol), and the mixture was heated at 50 °C for half an hour.<sup>45</sup> The excess acetyl chloride was removed *in vacuo* to afford a crystalline mass which was recrystallized from ethanol (3.2 g, ca. 100%), m.p. 291–293 °C;  $\delta_{\text{H}}$  1.22 (4 H, br d,  $J$  7.2), 1.42 (2 H, dd,  $J$  8.7 and 0.9), 1.71 (2 H, d,  $J$  8.7), 1.79 (4 H, br d,  $J$  7.2), 2.31 (6 H, s) and 3.27 (4 H, s);  $\delta_{\text{C}}$  20.65, 26.02, 40.85, 48.97, 153.66, 138.22 and 169.08;  $m/z$  326 ( $\text{M}^+$ ).

**Reaction of Dialkyl Ethers with NO<sub>2</sub>.**—*General procedure.* The dimethyl ether **1a** (270 mg, 1.0 mmol) was added to dichloromethane (10 cm<sup>3</sup>) under an argon atmosphere in a 100 cm<sup>3</sup> flask equipped with Teflon needle valve (Schlenk adapter). The flask was cooled in a dry ice–acetone bath (approx. –78 °C) and a cooled solution of NO<sub>2</sub> in dichloromethane (10 cm<sup>3</sup>, 0.2 mol dm<sup>-3</sup>) was added under an argon atmosphere. The solution which immediately turned deep orange was warmed to room temperature. After 5 min it resulted in a clear pale yellow solution. The head gases were transferred to an evacuated gas phase IR cell (5-cm path length). The IR spectrum thus recorded showed the characteristic strong NO stretching frequencies<sup>11</sup> of *cis*- and *trans*-MeONO at 1687, 1668, 1638, 1621 and 1611 cm<sup>-1</sup>. The gases from the IR cell were then transferred to an evacuated 1 cm quartz cuvette and the UV spectrum of the gases recorded. The sharp absorption bands observed in the region from 300 to 400 nm (characteristic of alkyl nitrites) were found to be identical with those recorded with an authentic sample<sup>46</sup> of methyl nitrite ( $\lambda_{\text{max}} = 302, 310, 319, 329, 339, 352, 365$  nm<sup>10</sup>). Removal of the solvent and gaseous methyl nitrite on a rotary evaporator gave crystalline quinone **1Q** (240 mg, 100%) which was analysed by GC, GC–MS and NMR spectroscopy.

A similar experiment was performed in a 1 cm quartz cuvette equipped with a sidearm and Teflon needle valve (Schlenk adapter) and charged with a solution of **1a** (2 cm<sup>3</sup>, 0.01 mol dm<sup>-3</sup>) in dichloromethane. The solution was cooled in a dry ice–acetone bath (approx. –78 °C), and a prechilled dichloromethane solution of NO<sub>2</sub> (2 cm<sup>3</sup>, 0.02 mol dm<sup>-3</sup>) was added under an argon atmosphere with the aid of an all-glass hypodermic syringe. The colour of the solution immediately turned orange and the UV–VIS spectrum was recorded [see Fig. 1(a)]. The reaction mixture was then warmed to room temperature. The mixture was cooled back to –78 °C and the UV–VIS spectrum was again recorded to show the presence of methyl nitrite and quinone **1Q** [see Figs. 1(b) and 1(c)].

**Reaction of Dioctyl Ether 1d with NO<sub>2</sub>.**—The ether **1d** (186.4 mg, 0.4 mmol) was treated according to the general procedure. Following the careful removal of the solvent *in vacuo*, the

residue (220 mg) was dissolved in deuterated chloroform. The NMR spectra thus recorded clearly indicated the presence of quinone **1** and octyl nitrite in the ratio 1 : 2. The octyl nitrite:<sup>15</sup>  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  323, 333, 345, 357, 371 and 385;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  2857, 2931, 2957, 1639, 1602, 1465 and 1375;  $\delta_{\text{H}}$  0.86 (3 H, t), 1.2–1.4 (12 H, m), 1.71 (2 H, quintet) and 4.67 (2 H, br t);  $\delta_{\text{C}}$  14.04, 22.62, 25.87, 29.14 (double intensity), 28.99, 31.75 and 68.46 (br).

**Reaction of <sup>18</sup>O-Labelled Dioctyl Ether 1d with NO<sub>2</sub>.**—**Preparation of <sup>18</sup>O-labelled dioctyl ether 1d.** Dimethyl ether **1a** (189 mg, 0.7 mmol) was dissolved in dry acetonitrile (3 cm<sup>3</sup>) and a solution of ceric ammonium nitrate (1.54 g, 2.8 mmol) in H<sub>2</sub><sup>18</sup>O (95% <sup>18</sup>O enriched, 1 g) was added all at once. The reaction mixture was left at room temperature for 10 min, and the doubly labelled quinone **1** (166 mg, 97%) was isolated according to the literature procedure;<sup>5</sup>  $m/z$  244 ( $\text{M}^+$ ). Zinc dust (3–4 g) was added to a yellow solution of labelled quinone **1** (100 mg, 0.41 mmol) in acetic acid (5 cm<sup>3</sup>), and the mixture heated for 2 min to yield a clear solution which was quickly filtered and cooled in an ice bath. The crystalline labelled hydroquinone **1** (H<sub>2</sub>Q) was filtered and dried *in vacuo* (94 mg, 93%). The <sup>18</sup>O-labelled hydroquinone **1** (100 mg, 0.41 mmol) was suspended in purified dry tetrahydrofuran (20 cm<sup>3</sup>), and potassium hydride (66 mg, 1.64 mmol) was added under an argon atmosphere. The reaction mixture was stirred for 10 min to produce a green solution. Octyl bromide (316 mg, 1.64 mmol) was added to this solution all at once and the mixture refluxed for 12 h. It was then cooled to room temperature and diluted with cold water (50 cm<sup>3</sup>). The organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 25 cm<sup>3</sup>). The combined organic layers were dried and filtered and, on evaporation of the solvent, gave crystalline **1d** which was recrystallized from dichloromethane–ethanol (156 mg, 81%);  $m/z$  470 ( $\text{M}^+$ ).

**Reaction of labelled dioctyl ether 1d with NO<sub>2</sub>.** Using the general procedure described above, a solution of <sup>18</sup>O-labelled **1d** (47 mg, 0.1 mmol) in dichloromethane (1 cm<sup>3</sup>) was treated with NO<sub>2</sub> in dichloromethane (1 cm<sup>3</sup>, 0.2 mol dm<sup>-3</sup>) prechilled to –78 °C under an argon atmosphere. GC–MS analysis of the reaction mixture showed that resultant quinone **1** was devoid of the isotopic labels;  $m/z$  240 ( $\text{M}^+$ ) [note that <sup>18</sup>O quinone **1** showed  $m/z$  244 ( $\text{M}^+$ )] whereas the octyl nitrite was fully <sup>18</sup>O-labelled;  $m/z$  131 ( $\text{M}^+ - \text{NO}$ ). [Note that unlabelled octyl nitrite showed  $m/z$  129 ( $\text{M}^+ - \text{NO}$ )] Following the careful removal of the solvent *in vacuo*, NMR analysis of the residue (53 mg) showed the presence of quinone **1** and octyl nitrite in the molar ratio 1 : 2.

**Reaction of Dimethyl Ether 1a with NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> and PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup>.**—A Schlenk flask was charged with nitrosonium tetrafluoroborate (23.4 mg, 0.2 mmol) in the dry box, and dichloromethane (10 cm<sup>3</sup>) then added under an argon atmosphere with the aid of a hypodermic syringe [Note that NO<sup>+</sup> salt does not dissolve in dichloromethane]. The slurry was cooled in a dry ice–acetone bath (approx. –78 °C), and dimethyl ether **1a** (54 mg, 0.2 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for 1 h to yield an orange-red solution of the radical cation (see Fig. 1 insert). The above solution was cooled in an ice bath (approx. 0 °C) and a prechilled solution of PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup> (121 mg, 0.2 mmol) in dichloromethane (2 cm<sup>3</sup>) was added to the reaction flask with

the aid of a hypodermic syringe. The colour of the reaction mixture immediately changed from red-orange to yellow, and analysis of the clear solution by UV spectroscopy indicated the presence of quinone and methyl nitrite. The solution was diluted with dichloromethane (25 cm<sup>3</sup>), washed with water (3 × 25 cm<sup>3</sup>), saturated aqueous sodium chloride (2 × 25 cm<sup>3</sup>), dried and filtered. Evaporation of the solvent afforded pure quinone (45 mg, 94%) which was analysed by GC-MS and NMR spectroscopy.

**Reaction of Radical Cation 1a<sup>•+</sup> with NO and PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup>.**—An orange-red solution of the crystalline radical cation 1a<sup>•+</sup> (121 mg, 0.2 mmol) in dichloromethane (20 cm<sup>3</sup>) was cooled in a dry ice-acetone bath under an argon atmosphere. Gaseous nitric oxide (purified by a passage through a NaOH tower and a cold trap cooled with dry ice-acetone) was then bubbled into the dichloromethane solution of the radical cation for 10 min with stirring. A prechilled solution of PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup> (121 mg, ca. 0.2 mmol) in dichloromethane (10 cm<sup>3</sup>) was added to the above reaction mixture with the aid of a hypodermic syringe. As the reaction mixture was warmed to room temperature the colour faded to yield a clear yellow solution. In the head gas methyl nitrite was detected by UV spectroscopy. The solvent was removed *in vacuo* and the reaction mixture was worked up as above to yield quinone 1 in excellent yield (47 mg, 98%, analysed by GC, GC-MS and NMR spectroscopy).

**Reaction of Radical Cation 1a<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> with PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup>.**—An orange-red solution of the crystalline radical cation 1a<sup>•+</sup>-SbCl<sub>6</sub><sup>-</sup> (121 mg, 0.2 mmol) in dichloromethane (20 cm<sup>3</sup>) was cooled in a dry ice-acetone bath under an argon atmosphere. A prechilled solution of PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup> (121 mg, ca. 0.2 mmol) in dichloromethane (10 cm<sup>3</sup>) was added to the reaction mixture with the aid of a hypodermic syringe. The colour of the reaction mixture changed from orange-red to yellow on warming to room temperature. Upon completion of the reaction (ca. 20 min), the solvent was removed *in vacuo* and the reaction mixture was worked up as described above to yield a 1:1 mixture of dimethyl ether 1a and quinone 1Q in excellent yield (50 mg) as quantified by GC and NMR spectroscopy. [Note that methyl nitrite was not detected in the head gas.]

A similar reaction was performed in deuteriated chloroform and the reaction mixture was directly analysed by NMR spectroscopy to show the presence of methyl nitrate<sup>27</sup> (2 equiv.)  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  3056, 2987, 2307, 1638, 1423, 1288, 1264, 1157, 995, 897 and 862;  $\delta_{\text{H}}$  4.03;  $\delta_{\text{C}}$  59.61. In addition, quinone 1Q (1 equiv.) and the dimethoxybenzene 1a (1 equiv.) were present.

**Reaction of Radical Cation 1a<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> with NO<sub>2</sub>.**—An orange-red solution of the crystalline radical cation 1a<sup>•+</sup>-SbCl<sub>6</sub><sup>-</sup> (121 mg, 0.2 mmol) in dichloromethane (20 cm<sup>3</sup>) was cooled in a dry ice-acetone bath under an argon atmosphere. A prechilled (approx. -78 °C) solution of NO<sub>2</sub> in dichloromethane (3 cm<sup>3</sup>, 0.2 mol dm<sup>-3</sup>) was added to the reaction mixture with the aid of a hypodermic syringe. There was a steady decrease in the absorption due to the radical cation ( $\lambda_{\max} = 516$  nm) with a concomitant increase in the absorption at 430 nm resulting in a yellow solution [compare: UV-VIS band at  $\lambda_{\max} = 430$  nm in Fig. 1(a)] which did not change with time (ca. 10 min) whilst kept cold (-78 °C). On warming to about 0 °C, a purple solution ( $\lambda_{\max} = 574$  nm) was obtained which eventually faded to yield a cloudy yellow solution on warming to room temperature. When the reaction mixture was allowed to stand for several hours at room temperature, a white precipitate separated from the solution. [UV analysis of the head gas indicated the presence of methyl nitrite.] The clear yellow solution was

decanted under an argon atmosphere, and the white precipitate washed several times with dichloromethane (3 × 10 cm<sup>3</sup>). Evaporation of the solvent from the combined washings and decanted yellow solution yielded quinone 1Q (ca. 80%) that was contaminated with a mixture of unidentified compounds. The white precipitate was identified as nitrosonium hexachloroantimonate (NO<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>)<sup>47</sup> by IR spectroscopy. The mixing of the insoluble precipitate with hexamethylbenzene in dichloromethane also yielded the intense red colour due to the EDA complex, *i.e.*, [hexamethylbenzene, NO<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>].<sup>47</sup> This reaction was repeated using a solution of radical cation 1a<sup>•+</sup> (600 mg, 1 mmol) in dichloromethane (25 cm<sup>3</sup>) with NO<sub>2</sub> (15 cm<sup>3</sup>, 0.2 mol dm<sup>-3</sup>) in dichloromethane. The cloudy reaction mixture thus obtained was cooled to 0 °C under an oxygen atmosphere, and 1,4-dimethoxybenzene (414 mg, 3 mmol) was added whilst maintaining the oxygen atmosphere. The reaction mixture was stirred for 1 h under an oxygen atmosphere, after which a clear yellow solution was obtained. The reaction mixture was diluted with water and the dichloromethane layer was washed with saturated aqueous sodium chloride. The organic layer was dried, filtered and the solvent evaporated off to yield a residue (690 mg) which was analysed by GC-MS, GC and NMR spectroscopy. The quinone 1Q, 2-nitro-1,4-dimethoxybenzene<sup>48</sup> and 1,4-dimethoxybenzene were present in the mole ratio 0.8:2:1. In addition, a number of unidentified products (< 5%) were noted. [Note that in presence of strong acid methyl nitrate acts as a nitrating agent;<sup>49</sup> and the reaction of dimethoxybenzene with NO<sup>+</sup> in presence of O<sub>2</sub> leads to 2-nitro-1,4-dimethoxybenzene.<sup>25</sup>]

**Reaction of 4-Methoxy-2,6-di-tert-butylphenol 13 with NO<sub>2</sub>.**—A solution of the methoxyphenol 13 (473 mg, 2 mmol) in dichloromethane (20 cm<sup>3</sup>) was cooled under an argon atmosphere in a dry ice-acetone bath (approx. -78 °C), and a cooled solution of NO<sub>2</sub> in dichloromethane (15 cm<sup>3</sup>, 0.2 mol dm<sup>-3</sup>) was added. The reaction mixture, which initially became blue-green, rapidly changed to yellow on being warmed to room temperature within a ca. 5 min period, and a clear solution was obtained. The gases from the cuvette were then transferred to an evacuated gas IR cell (5 cm path length), and the IR spectrum thus recorded showed a characteristic sharp band at 1875 cm<sup>-1</sup> and a pair of broad bands centred at 1845 and 1906 cm<sup>-1</sup> characteristic of the P, Q and R branches of nitric oxide (NO).<sup>20</sup> In addition, the characteristic strong NO stretching frequencies of methyl nitrite<sup>11</sup> (1687, 1668, 1633, 1621 and 1611 cm<sup>-1</sup>) were observed. The gases from the IR cell were then transferred to an evacuated 1 cm quartz cuvette, and the UV spectrum of the gases recorded. Three sharp absorption bands at 204, 214 and 226 nm<sup>50</sup> were observed and found to be identical with that recorded with authentic sample of purified NO. Additionally, the appearance of a set of bands in the region 300–400 nm was diagnostic of alkyl nitrites, and these were found to be identical with that recorded with an authentic sample of methyl nitrite. Removal of the solvent on a rotary evaporator gave crystalline quinone 13 (640 mg, 100%) analysed by GC, GC-MS and NMR spectroscopy.

**Reaction of Dimethyl Ether 1a with Sodium Nitrite and Hydrochloric Acid.—General procedure.** Sodium nitrite (140 mg, 2 mmol) was added to a solution of dimethyl ether 1a (270 mg, 1 mmol) in dichloromethane (10 cm<sup>3</sup>) in a 100 cm<sup>3</sup> flask equipped with a sidearm. The flask was purged with O<sub>2</sub>, stoppered with a rubber septum and an oxygen-filled balloon attached to the sidearm. The flask was cooled in an ice-acetone bath (approx. -10 °C) and 2 drops of concentrated hydrochloric acid were added. The reaction mixture was stirred for 1 h and at the end of this time a clear yellow solution was obtained which was dried over anhydrous magnesium sulfate



and filtered. Removal of the solvent *in vacuo* afforded pure quinone 1Q in almost quantitative yield (238 mg).

**Reaction of Dimethyl Ether 1a with Ferric Chloride and PPN<sup>+</sup>-NO<sub>3</sub><sup>-</sup>.**—A solution of dimethyl ether 1a (270 mg, 1.0 mmol) and PPN<sup>+</sup>NO<sub>3</sub><sup>-</sup> (1.21 g, 2 mmol) in dichloromethane (20 cm<sup>3</sup>) in a 100 cm<sup>3</sup> flask equipped with a Teflon needle valve (Schlenk adapter) was cooled, under an argon atmosphere, in an ice-acetone bath (approx. -10 °C). A solution of ferric chloride (325 mg, 2 mmol) in dry acetonitrile (5 cm<sup>3</sup>) was added under an argon atmosphere and the colour of the solution turned deep orange, which, upon warming to room temperature (*ca.* 10 min), resulted in a clear yellow solution. The reaction mixture was diluted with dichloromethane (50 cm<sup>3</sup>) and washed several times with water (3 × 25 cm<sup>3</sup>). The organic layer was dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent *in vacuo* gave the crystalline quinone 1 (235 mg, 98%) as analysed by GC, GC-MS and NMR spectroscopy.

**Quinones.**—The product quinones listed in Table 1 were found to be identical with commercial samples or with authentic samples prepared by literature procedures. The characteristic data are: 1,4:5,8-Dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone<sup>12</sup> 1; m.p. (sublimes at 200–230 °C);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2995, 2971, 2952, 2875, 1648vs, 1638s, 1569, 1330, 1272, 1210, 1119, 875, 760 and 741;  $\delta_{\text{H}}$  1.13 (4 H, br d), 1.34 (2 H, d, *J* 8.7), 1.57 (2 H, d, *J* 8.7), 1.86 (4 H, br d) and 3.42 (4 H, br s);  $\delta_{\text{C}}$  24.79, 40.19, 48.08, 150.97 and 181.97; *m/z* 240 (M<sup>+</sup>). 1,4:5,8-Diethano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone<sup>12</sup> 2; m.p. (sublimes at 280–340 °C);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2959, 2947, 2913, 2870, 1648vs, 1692, 1597, 1356, 1304, 1238, 1146, 818 and 745;  $\delta_{\text{H}}$  1.28 (8 H, d, *J* 7.5), 1.68 (8 H, d, *J* 7.5) and 3.32 (4 H, s);  $\delta_{\text{C}}$  25.28, 26.34, 147.24 and 187.40; *m/z* 268 (M<sup>+</sup>). 1,4-Ethano-5,8-methano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone<sup>12</sup> 3; m.p. (sublimes at 220–240 °C);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2951, 2869, 1643vs, 1578, 1451, 1354, 1325, 1289, 1272, 1230, 1206, 1194, 1148, 1111, 1014, 917, 895, 866, 839, 781, 745 and 672;  $\delta_{\text{H}}$  1.16 (2 H, sym m), 1.23 (4 H, sym m), 1.34 (1 H, sym m), 1.58 (1 H, sym d), 1.65 (4 H, sym m), 1.87 (2 H, sym m), 3.27 (2 H, s) and 3.44 (2 H, br s);  $\delta_{\text{C}}$  24.98, 25.08, 25.35, 26.27, 40.53, 47.79, 147.28, 150.86 and 181.73; *m/z* 254 (M<sup>+</sup>). 5,8-Ethano-1,4-methano-1,2,3,4,5,8-hexahydro-9,10-anthraquinone<sup>12</sup> 4; m.p. 148 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2973, 2956, 2973, 1645vs, 1576, 1333, 1321, 1291, 1270, 1228, 1186, 1156, 1142, 1114, 1093, 882, 832, 781, 745 and 703;  $\delta_{\text{H}}$  1.14 (2 H, sym m), 1.28 (1 H, sym m), 1.30 (2 H, sym m), 1.39 (2 H, sym m), 1.52 (1 H, sym m), 1.84 (2 H, sym m), 3.385 (2 H, s), 5.25 (2 H, s) and 6.33 (2 H, t);  $\delta_{\text{C}}$  24.63, 24.99, 33.62, 40.46, 47.85, 133.93, 147.83, 150.70 and 181.21; *m/z* 252 (M<sup>+</sup>). 1,4:5,8-Diethano-1,2,3,4,5,8-hexahydro-9,10-anthraquinone<sup>12</sup> 5; m.p. (sublimes at 180–220 °C);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3070, 3050, 2945, 2869, 2925, 1642vs, 1608, 1587, 1452, 1355, 1326, 1304, 1273, 1233, 1141, 1014, 817, 716, 687 and 645;  $\delta_{\text{H}}$  1.15–1.50 (8 H, m), 1.66 (4 H, t), 3.29 (2 H, s), 4.32 (2 H, s) and 6.37 (2 H, AB system,  $\Delta\nu_{\text{AB}}, J_{\text{AB}}$  3);  $\delta_{\text{C}}$  24.60, 25.19, 25.34, 26.38, 33.70, 133.92, 146.89, 147.56 and 180.93; *m/z* 266 (M<sup>+</sup>). 1,4-Methano-1,2,3,4,5,6,7,8-octahydro-9,10-anthraquinone<sup>12</sup> 6; m.p. 78–79 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2992, 2946, 2880, 1642vs, 1593, 1454, 1424, 1357, 1328, 1286, 1272, 1193, 1121, 1103, 843, 730 and 710;  $\delta_{\text{H}}$  1.10 (2 H, sym m), 1.31 (1 H, d, *J* 8.7), 1.53 (1 H, dt, *J* 9 and 1.7), 1.61 (4 H, quintet, *J* 3), 1.84 (2 H, sym m), 2.34 (4 H, sym m) and 3.40 (2 H, s);  $\delta_{\text{C}}$  21.12, 22.49, 25.03, 40.57, 47.41, 141.48, 151.03 and 184.70; *m/z* 228 (M<sup>+</sup>). 6,7-Dimethyl-1,4-methano-1,2,3,4-tetrahydrodimethyl-5,8-naphthoquinone<sup>51</sup> 7; m.p. 68–70 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2997, 2973, 2950, 2873, 1642vs, 1595, 1451, 1376, 1334, 1290, 1273, 1224, 1109, 947 and 784;  $\delta_{\text{H}}$  1.08 (2 H, sym m), 1.30 (1 H, d), 1.53 (1 H, sym m), 1.83 (2 H, sym m), 1.92 (6 H, s) and 3.41 (2 H, br s);  $\delta_{\text{C}}$  12.05, 25.06, 40.68, 47.34, 139.95, 150.97 and 184.51; *m/z* 202 (M<sup>+</sup>). 1,2,3,4,5,6,7,8-

octahydro-9,10-anthraquinone<sup>12</sup> 8; m.p. 183–184 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2944, 2889, 2870, 1640vs, 1619, 1465, 1423, 1358, 1295, 1188, 973, 808, 707 and 688;  $\delta_{\text{H}}$  1.60 (8 H, sym m) and 2.32 (8 H, sym m);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.08, 22.37, 141.68 and 187.38; *m/z* 216 (M<sup>+</sup>). Tetraethyl-1,4-benzoquinone<sup>52</sup> 9; m.p. 54–55 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2973, 2938, 2879, 1642vs, 1613, 1460, 1329, 1291, 1254, 1236, 1060, 1052, 962, 841 and 753;  $\delta_{\text{H}}$  1.01 (12 H, t, *J* 7.5) and 2.42 (8 H, q, *J* 7.5);  $\delta_{\text{C}}$  13.95, 19.63, 144.97 and 187.50; *m/z* 220 (M<sup>+</sup>). Duroquinone 10; m.p. 110–112 °C (Aldrich). 2,6-Di-*tert*-butyl-1,4-benzoquinone 13; m.p. 65–67 °C (Aldrich). 2,3,6-Trimethyl-1,4-benzoquinone<sup>53</sup> 14; m.p. 31–32 °C;  $\delta_{\text{H}}$  1.88 (3 H, s), 1.90 (3 H, s), 1.92 (3 H, d, *J* 1.5) and 6.43 (1 H, q, *J* 1.5);  $\delta_{\text{C}}$  11.84, 12.14, 15.67, 132.83, 140.50, 140.66, 145.11, 187.21 and 187.59.

**Spectral Measurement of the Reaction of 1a<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> with NO.**—A solution of cation radical 1a<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> in dichloromethane (4 cm<sup>3</sup>, 2 × 10<sup>-4</sup> mol dm<sup>-3</sup>) in a 1 cm quartz cuvette equipped with a sidearm and Teflon needle valve (Schlenk adapter) was cooled in a dry ice-acetone bath (approx. -78 °C) under an argon atmosphere. Gaseous nitric oxide (purified by a passage through a NaOH tower and a cold trap cooled with dry ice-acetone) was then bubbled into the dichloromethane solution of the cation radical for 5 min. The UV-VIS spectrum of the pale purple-yellow solution was recorded at -78 °C to show only the presence of an absorption band at  $\lambda_{\max} = 370$  nm (see Fig. 3). The orange colour ( $\lambda_{\max} = 518$  nm) of the solution progressively intensified on warming the solution, and the absorption band at 370 nm completely disappeared at 40 °C (see Fig. 3). This process was completely reversible over multiple cooling-warming cycles.

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