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Selective Nitration *versus* Oxidative Dealkylation of Hydroquinone Ethers with Nitrogen Dioxide

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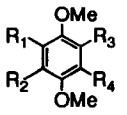
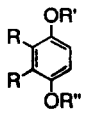
Abstract: Various alkyl-substituted *p*-dialkoxybenzenes (ArH) react readily with nitrogen dioxide (NO_2) in dichloromethane solution via either nitration ($ArNO_2$) or oxidative dealkylation to quinones (Q). Spectral transients indicate that these coupled processes proceed from the dialkoxybenzene radical cation ($ArH^{+\cdot}$) formed as the common reactive intermediate from electron-transfer in the disproportionated precursor [ArH, NO^+] NO_3^-. In fast subsequent steps, $ArH^{+\cdot}$ undergoes homolytic coupling with NO_2 (which leads to aromatic nitration) and nucleophilic attack of NO_3^- (which results in oxidative dealkylation). As such, the competition between nitration and oxidative dealkylation is effectively modulated by solvent polarity and added nitrate.

Introduction

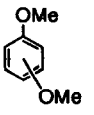
Aromatic nitration is conventionally carried out with nitric acid, either alone or in combination with either Bronsted or Lewis acids.[1] Different types of aromatic compounds, including various anthracenes, naphthalenes, (poly)methylbenzenes, and alkoxybenzenes, also react readily with nitrogen dioxide (NO_2) in nonpolar solvents such as chloroform, dichloromethane, nitromethane, etc.[2] Aromatic nitration with this (gaseous) reagent under such aprotic conditions thus represents a potentially useful synthetic methodology, especially for acid-sensitive functionalities. However, the ambiguous behavior of some types of aromatic donors toward nitrogen dioxide is particularly intriguing, and we believe it could provide the key to our understanding of this simple, yet versatile reagent.[3] For example, there is an early report [4] that *p*-dimethoxybenzene is quantitatively *nitrated* by nitrogen dioxide in carbon tetrachloride at 25 °C. On the other hand, we recently showed[5] that the tetramethyl analogue is oxidatively *demethylated* by nitrogen dioxide under essentially the same reaction conditions to form duroquinone, also in quantitative yield. In order to examine the dichotomy between aromatic nitration and quinone formation, we prepared three homologous series of dialkoxybenzene derivatives for study, viz.



I



II



III

where R_1, R_2, R_3 and R_4 are either methyl or hydrogen and R and R' and R" are hydrogen or alkyl groups.

Earlier, Addison and Sheldon qualitatively noted transient yellow (orange) colors when various aromatic compounds were exposed to nitrogen dioxide (and its equilibrium dimer dinitrogen tetroxide).[6] Our subsequent spectroscopic (UV-vis, IR and time resolved) studies established that the colorations arose from the nitrosonium EDA or electron donor-acceptor complexes [ArH, NO^+] that was formed via the arene-induced disproportionation of nitrogen dioxide, i.e.[7]

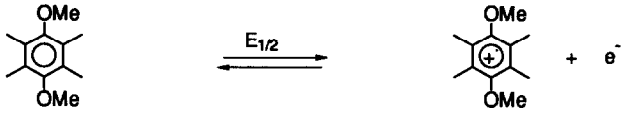
$$ArH + 2NO_2 \underset{}{\overset{K_{DISP}}{\rightleftharpoons}} [ArH, NO^+]\,NO_3^- \qquad (1)$$

The magnitude of the disproportionation constant K_{DISP} in eq 1 was strongly dependent on the aromatic donor strength, as evaluated by the ionization potential (gas phase) or oxidation potential (solution).[8] Accordingly in this study, electron-donor properties of the dialkoxybenzenes in series **I, II** and **III** were first assessed by transient electrochemistry. Each series of aromatic donors was then subjected to nitrogen dioxide in dichloromethane solution (in the dark) under a standard set of reaction conditions. The workup of the reaction mixture involved the convenient removal of the nitrogen oxides and low-boiling solvent *in vacuo*, and it was usually followed by simple recrystallization of the product residue.

Results

I. Dimethoxybenzenes (I) as Electron Donors.

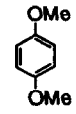
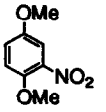
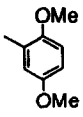
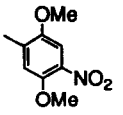
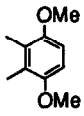
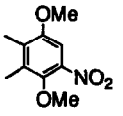
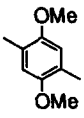
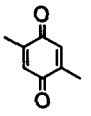
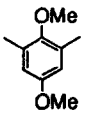
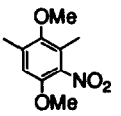
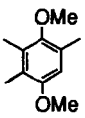
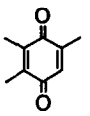
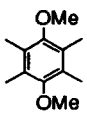
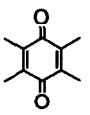
The homologous *p*-dimethoxybenzenes in series **I** (Table I) were oxidized electrochemically at a platinum electrode as 5 x 10^{-3} M solutions in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Reversible cyclic voltammograms (CV) of the dimethyl ethers **Ia-f** were consistently attained at scan rates of v = 0.1 V s^{-1}, and they all showed anodic / cathodic peak current ratios of $i_a / i_c = 1.0$ (theoretical) at 25 °C. The calibration of the CV peaks with ferrocene then indicated the reversible oxidation potentials ($E_{1/2}$) for the production of the cation radicals via the 1-electron redox couple, i.e.



(2)

The values of $E_{1/2}$ in Table I (column 2) followed an unusual trend with the number of methyl substituents. Thus the tetramethyl derivative **Ig** was oxidized at the most positive potential[9] -- similar to that of the (least methylated) parent **Ia.** On the other hand, the intermediate 2,5-dimethyl analogue **Id** was the best electron donor, as judged by its (most negative) value of the $E_{1/2}$ = 1.02 V. Indeed, the substitution *pattern* and not the *number* of methyl groups appeared to be the most important determinant for $E_{1/2}$. In this regard, the donor behavior of the (polymethyl)dimethoxybenzenes was quite distinct from that of the (polymethyl)benzenes, in which previous studies showed that $E_{1/2}$ decreases monotonically with the number of methyl substituents (independent of the substitution pattern).[8]

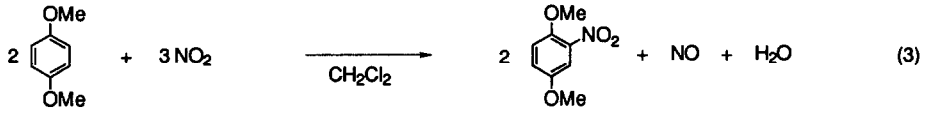
Table I. Methyl-substituted *p*-Dimethoxybenzenes (I) as Electron Donors. The Dichotomy between Nitration and Oxidative Demethylation with Nitrogen Dioxide.[a]

	Donor	$E_{1/2}$ (E_p)[b]	Products[c] (%)
Ia.		1.348 (1.438)	 (100)
Ib.		1.160 (1.250)	 (100)
Ic.		1.142 (1.177)	 (100)
Id.		1.019 (1.084)	 (89)
Ie.		1.297 (1.362)	 (100)
If.		1.258 (1.335)	 (80)
Ig.		1.48[d] (1.567)	 (100)

[a] In dichloromethane solution under an argon atmosphere (in the dark). [b] V vs. SCE at 25 °C. In parenthesis, anodic peak potential at v = 0.1 V s^{-1}. [c] At -78 °C to 25 °C (see text). [d] Extrapolated values from the linear correlation of E_p vs. $E_{1/2}$ (see Experimental Section).

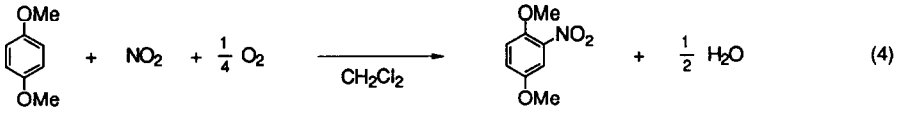
II. Nitration and Demethylation of Dimethoxybenzenes (I) with Nitrogen Dioxide

When a solution of *p*-dimethoxybenzene (**Ia**) in dichloromethane at -78 °C was treated under an argon atmosphere with a cold dichloromethane solution of nitrogen dioxide (1.5 equiv.), the solution immediately turned bright yellow. The color faded quickly, and after 2 min, the solution was warmed to room temperature. Spectral analysis of the head gas led to the identification of nitric oxide by its characteristic IR and UV-vis absorptions at υ_{NO} = 1875 cm^{-1} and λ_{NO} = 204, 214, and 226 nm, respectively.[10,11] Removal of the solvent (together with nitric oxide) from the reaction mixture *in vacuo* afforded a quantitative yield of 2,5-dimethoxynitrobenzene as yellow crystals, i.e.



(3)

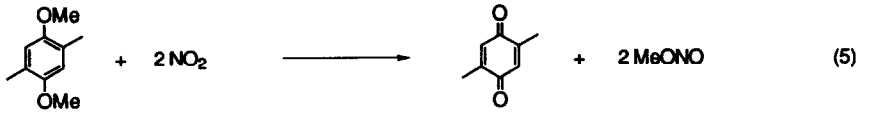
which were essentially free of organic impurities (<1 %) by ^1H NMR and GC-MS analysis.[4] Moreover, the complete utilization of the nitrogen oxides was possible in eq 3 based on the rapid autoxidation of NO.[12] Thus equimolar amounts of dimethoxybenzene and nitrogen dioxide when treated in dichloromethane in the presence of dioxygen led to a quantitative yield of the same nitration product according to the stoichiometry in eq 4 (see Experimental Section).



(4)

Spectral (IR) analysis of the head gas revealed that no residual nitrogen oxide (either NO_2 or NO) was present.

The mono-methyl derivative **Ib** reacted with nitrogen dioxide in much the same manner as *p*-dimethoxybenzene, described above. The specificity of the nitration was shown by the production of a single isomer (Table I) in essentially quantitative yields. Contrastingly, the three isomeric dimethyl derivatives **Ic**, **Id**, and **Ie** showed quite distinctive behavior toward nitrogen dioxide. Thus the 2,3- and 2,6-dimethyl analogues were quantitatively nitrated to the mono-nitro derivatives depicted in Table I. In each of these cases, IR and UV-vis spectral analysis established nitric oxide as the sole volatile nitrogen oxide, in accord with the stoichiometry in eq 2. The 2,5-dimethyl analogue **Id** qualitatively reacted with nitrogen dioxide like the other methylated derivatives of *p*-dimethoxybenzene insofar as the temporal progression of visible color changes. However, the IR and UV-vis spectral analysis of the head gas showed the presence of only minor amounts of nitric oxide. In its place were observed the IR bands[13] of methyl nitrite at υ_{MeONO} = 1611, 1621, 1638, 1668, and 1687 cm^{-1} and also its diagnostic vibrational fine structure in the UV-vis spectrum[14] at λ_{MeONO} = 301, 306, 310, 318, 319, 340, 351, 365, and 388 nm. The simple workup of the reaction mixture by removal of the solvent (together with the volatile methyl nitrite) *in vacuo* afforded 2,5-dimethyl-1,4-benzoquinone in 89 % yield,[15] i.e.

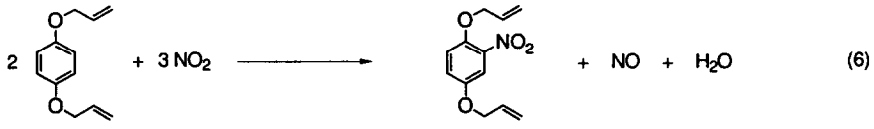


[Note: the stoichiometry in eq 5 for the oxidative dealkylation of dialkoxybenzenes was established earlier.[5]]

Oxidative dealkylation of the *p*-dimethoxybenzene moiety as described in eq 5 was also observed with the trimethyl- and tetramethyl analogues, **If** and **Ig**, respectively. In both cases, IR and UV-vis spectral analysis established the formation of methyl nitrite, and the removal of the solvent *in vacuo* led to trimethyl- and tetramethyl-*p*-benzoquinone [5] in 80 and 100 % yields, respectively (see Experimental Section).

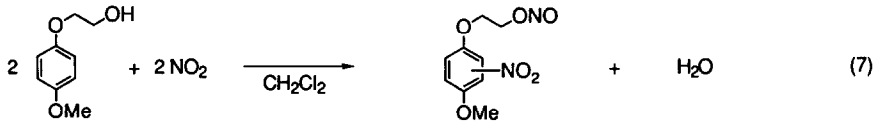
III. Nitration of *p*-Dialkoxybenzene Donors (II) with Nitrogen Dioxide.

The *p*-dialkoxybenzenes in series **II** were analogues of either the parent dimethoxybenzene (**Ia**) or the 2,3-dimethyl derivative (**Ic**). As such, they were treated with nitrogen dioxide (1.5 equiv.) in dichloromethane solution at -78 °C, and the yellow (orange) mixtures allowed to warm to room temperature under an argon atmosphere. The symmetrical dialkoxybenzenes **Ia** and **IIb-c** all gave a single nitrated derivative in quantitative yields (see Table II). It is noteworthy that the diallyl derivative **IIc** underwent ring nitration exclusively with the terminal double bonds intact, i.e.



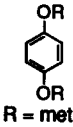
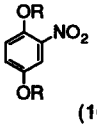
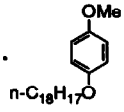
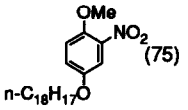
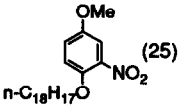
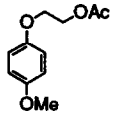
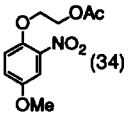
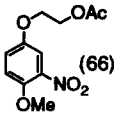
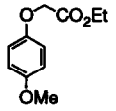
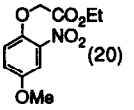
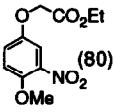
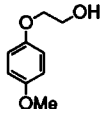
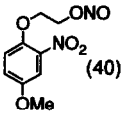
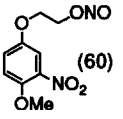
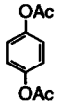
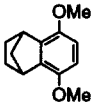
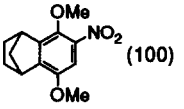
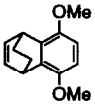
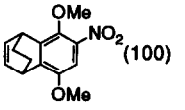
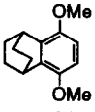
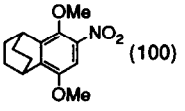
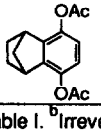
[Note that ordinarily olefins are readily nitrated or oxidized by nitrogen dioxide.[16]]

The unsymmetrical donors (Table II, entries 4-7) each gave almost statistical mixtures of the two nitro-isomers in quantitative yield. The reaction of 2-hydroxyethyl-(4-methoxyphenyl) ether was somewhat more complex. On the treatment of 1 equiv. of this aromatic donor (**IIg**) with 2 equiv. of nitrogen dioxide, all the nitrogen oxides were consumed and a quantitative yield of a mixture of the two nitroarenes was obtained. In addition to ring nitration, the sidechain alcohol was also transformed into the nitrite, i.e.



The series of fused ring ethers (**IIi-k**) were prepared by the Diels-Alder reaction of benzoquinone with either cyclopentadiene or cyclohexadiene, followed by reduction of the olefin, aromatization and alkylation.[5] These polyalkyldimethoxybenzenes reacted with nitrogen dioxide to afford quantitative yields of the mono-nitro derivative (see Table II). The high preference for aromatic nitration relative to olefin nitration / oxidation was again demonstrated with the ethano-bridged dimethoxydihydronaphthalene (Table II, entry 10), in which the double bond remained intact during quantitative ring nitration. It is interesting to note that the di-acetate **IIh** of

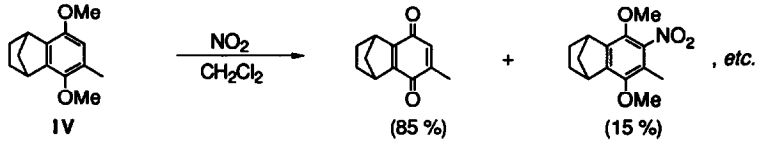
Table II. Nitration of *p*-Dialkoxybenzenes (II) with Nitrogen Dioxide.[a]

p-Dialkoxybenzene		$E_{1/2}$	Nitration Product (%)	
				
Ia.	R = methyl	1.348		(100)
IIb.	R = isopropyl	1.191		(100)
IIc.	R = allyl	1.334		(100)
IId.		1.300		
IIe.		1.372		
IIf.		1.446		
IIg.		1.362		
IIh.		(2.133)[b]	—[c]	
III.		1.172		
IIj.		1.161		
IIk.		1.141		
IIm.		(2.040)[b]	—[c]	

[a] As in Table I. [b] Irreversible cyclic voltammogram at v = 0.1 Vs^{-1}. Anodic peak potential in parenthesis.
[c] Diacetate recovered intact.

the parent *p*-hydroquinone did not react with nitrogen dioxide under these conditions; and the diester **IIm** of the fused ring analogue was similarly unreactive. In both cases, the cyclic voltammetric anodic waves were significantly shifted ($\Delta E_p \sim 700$ mV) to higher positive potentials relative to those of the corresponding dimethyl ethers **Ia** and **IIi**, respectively.

In contrast to the quantitative nitration of the fused ring ether **IIi**, the mono-methyl analogue **IV** (prepared via methyl-*p*-benzoquinone), yielded the single nitro product in only 15 % yield. The remainder of **IV** was accounted for as the quinone derived from oxidative demethylation, i.e.



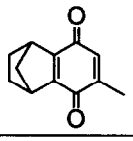
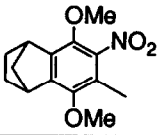
(8)

Furthermore, the 7-methoxymethyl derivative (**IVa**) of compound **IV** (eq 8) upon treatment with nitrogen dioxide in dichloromethane at -78 °C yielded the corresponding methoxymethylquinone (25 %) and the same nitro product (75 %) described in eq 8.

IV. Intramolecular and Intermolecular Competition between Nitration/Dealkylation of Dialkoxybenzenes with Nitrogen Dioxide.

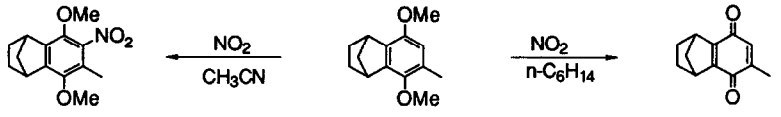
The solvent effect on the (intramolecular) competition between nitration and demethylation in eq 8 was examined in *n*-hexane and acetonitrile, since this pair of solvents represented the opposed extremes of polarity, measured either as Gutman donor number (DN)[17] or the Reichardt-Dimroth E_T values.[18] First, the reaction of 2,3,5-trimethyl-1,4-dimethoxybenzene (**If**) with nitrogen dioxide was studied qualitatively in the following way. A cold (-78 °C) 0.1 M solution of the arene was added by cannula under argon pressure to a dichloromethane solution of nitrogen dioxide (2 equiv., 0.2 M) at -78 °C, and the solution stirred at this temperature for 20 min. in the dark. The solvent and nitrogen oxides were removed *in vacuo* at low temperature, and then while allowing the solution to warm to 0 °C. GC-MS and ^{1}H NMR analysis of the crude residue indicated that 67 % of **If** was consumed. The predominant formation of the quinone (80 %), together with traces of other products including the ring- and sidechain nitro derivatives was noted. The same reaction in hexane solution at -78 °C afforded a similar distribution of products at a slightly slower rate (35 % conversion in 20 min.). The reaction performed in acetonitrile at -35 °C led to the complete consumption of **If** in less than 8 min, and equal amounts of the products of nuclear nitration, sidechain nitration and the quinone. [The reaction was carried out at this temperature owing to the higher melting point of acetonitrile.] The concentration of nitrogen dioxide was important. Thus the rapid mixing of equal volumes of a cold 1.0 M solution of nitrogen dioxide in acetonitrile with a cold 0.1 M acetonitrile solution of **If** immediately produced dinitrogen trioxide (as noted by its green color). The solvent and nitrogen oxides were removed *in vacuo* after 2 min. at -30 °C. The crude residue consisted mainly of the nitroaromatic (89 %) along with the quinone (7 %) (see Experimental Section).

Table III. Solvent and Salt Effects on the Intramolecular Competition in Nitration / Dealkylation with Nitrogen Dioxide[a]

Solvent	E_T	Additive	Products (%)[b]	
				
n-Hexane[c]	0.00	none	84	16
Dichloromethane[d]	0.31	none	80	20
Nitroethane[d]	0.40	none	79	21
Acetonitrile[e]	0.46	none	20	80
Acetonitrile[e, f]	0.46	$Bu_4N^+ PF_6^-$	13	87
Acetonitrile[e, g]	0.46	$PPN^+ NO_3^-$	72	28

[a]In solutions containing 0.2 M III. [b]Ratio of products. Conversion > 90 % for each reaction. Combined yield > 95 % in all reactions. [c]With NO_2 (0.1 M, 2 equiv.) at -40 °C for 10 min. [d]With NO_2 (0.1 M, 2 equiv.) at - 78 °C for 2 min. then warmed to 25 °C. [e]With NO_2 (1.0 M, 20 equiv.). [f]With added $Bu_4N^+ PF_6^-$ (20 equiv.) at -40 °C for 2 min. [g] With added $PPN^+ NO_3^-$ (8 equiv.) at -40 °C for 2 min.

The intramolecular competition between nitration and demethylation was examined quantitatively by treating the tetrahydronaphthalene analogue **IV** (eq 8) under a standard set of conditions described in Table III. Thus entries 1-4 establish the dramatic changeover from predominant demethylation to predominant nitration with increasing solvent polarity, i.e.

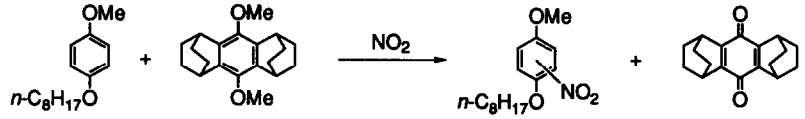


(9)

More striking is the specific anion effect in which added nitrate (entry 6) diverted the course of reaction from nitration to dealkylation, but hexafluorophosphate (entry 5) was without significant effect.[19]

Intermolecular competition between nitration and demethylation was examined with pairs of substrates which were selected to react at more or less the same rate with nitrogen dioxide. We initially chose the substrates

with exactly the same oxidation potential which displayed different product selectivity in dichloromethane. Thus a cold (-78 °C) dichloromethane solution of nitrogen dioxide (0.2 M, 1 equiv.) was added to a cold (-78 °C) dichloromethane solution containing 1 equiv. each of 9,10-dimethoxy-1,4:5,8-diethanooctahydroanthracene ($E_{1/2}$ = 1.30 V) and 1-octyloxy-4-methoxybenzene ($E_{1/2}$ = 1.30). After 2 min, the temperature was raised to 25 °C and the yellow mixture stirred for 15 min. NMR and GC-MS analysis of the reaction crude indicated that 0.25 equiv. of a mixture of 2- and 3-nitro-4-octyloxyanisole and 0.55 equiv. of 1,4:5,8-diethanooctahydroanthraquinone were formed, whilst the remainder of each substrate was unchanged.[20] The same competition was then carried out in acetonitrile solution which was initially at -40 °C and then warmed to room temperature for 15 min. GC-MS and NMR analysis indicated that the principal product was a mixture of 2- and 3-nitro-4-octyloxyanisole (0.65 equiv.) with less than 0.01 equiv. of the 1,4:5,8-diethanooctahydroanthraquinone formed.

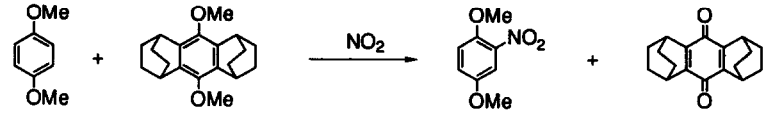


(10)

(1.00) (1.00) CH_2Cl_2 (0.25) (0.55)

CH_3CN (0.65) (< 0.01)

A second series of competition reactions were performed under the same conditions with substrates of different oxidation potentials. Thus the treatment of nitrogen dioxide (1 equiv.) with 1,4-dimethoxybenzene (1 equiv., $E_{1/2}$ = 1.35 V) and 9,10-dimethoxy-1,4:5,8-diethanooctahydroanthracene (1 equiv., $E_{1/2}$ = 1.30 V) in dichloromethane yielded less than 0.05 equiv. of 2,5-dimethoxynitrobenzene and 0.5 equiv. of 1,4:5,8-diethanooctahydroanthraquinone. When this reaction was repeated in acetonitrile solution, the selectivity was reversed. Thus, 2,5-dimethoxynitrobenzene was the exclusive product (0.65 equiv.) with less than 0.01 equiv. of the 1,4:5,8-diethanooctahydroanthraquinone formed.



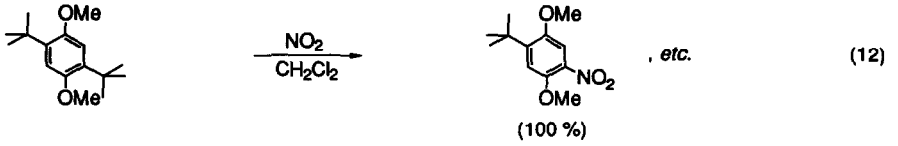
(11)

(1.00) (1.00) CH_2Cl_2 (< 0.05) (0.50)

CH_3CN (0.65) (< 0.01)

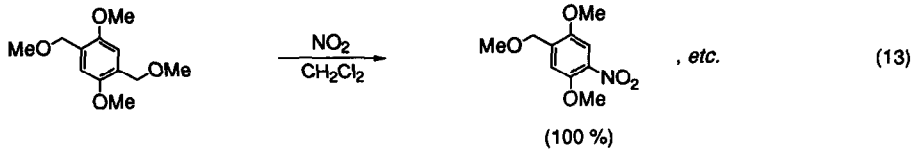
V. Nitro-dealkylation of Dialkoxybenzenes with Nitrogen Dioxide.

Owing to the strongly divergent behaviour of the 2,5- and 2,6-dimethyl isomers **Id** and **Ie** toward nitrogen dioxide in Table I (entries 4 and 5), we examined the steric effect with the corresponding *tert*-butyl homologues. Indeed, the behaviour of the isomeric 2,5- and 2,6-di-*tert*-butyldimethoxybenzene toward nitrogen dioxide was again quite selective. Thus whilst the 2,6 analogue afforded nitroaromatic in excellent yield, the 2,5 isomer suffered exclusive nitro-dealkylation, i.e.



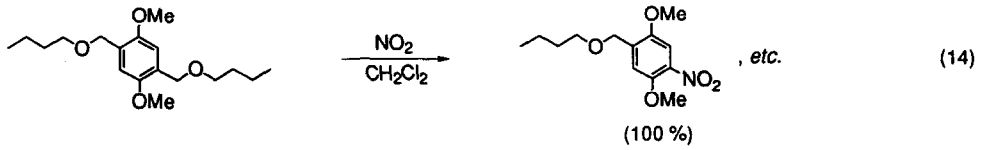
(12)

When both *tert*-butyl groups were replaced with a pair of methoxymethyl substituents, a similar nitro-dealkylation occurred, i.e.



(13)

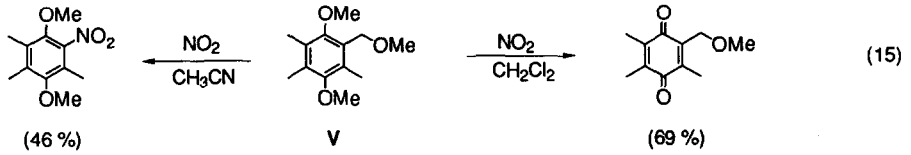
Similarly, the treatment of the *n*-butoxymethyl analogue, 2,5-di-*n*-butoxymethyl-1,4-dimethoxybenzene with nitrogen dioxide in dichloromethane led exclusively to the mono-nitro product via nitro-dealkylation, i.e.



(14)

For the fate of the cleaved group, ^{1}H NMR analysis was consistent with the sidechain product being *n*-butoxymethyl nitrate (or nitrite, see Experimental Section.)

An interesting intramolecular competition between nitro-dealkylation and oxidative dealkylation was observed with methoxymethyl(trimethyl)-*p*-dimethoxybenzene **V**. Thus the treatment of **V** with nitrogen dioxide in dichloromethane led to the quinone (69 %) in a manner similar to the tetramethyl analogue **Ig** (Table I). On the other hand, when the same reaction was repeated with nitrogen dioxide in acetonitrile at -35 °C, nitro-dealkylation was the predominant result, i.e.[21]

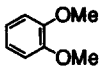
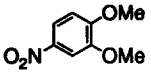
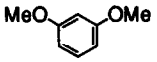
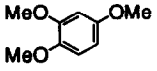
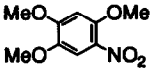
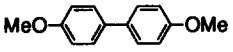
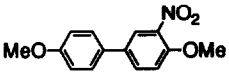
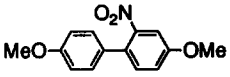
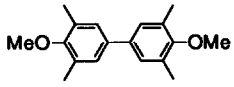
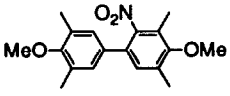


(15)

VI. Aromatic Radical Cations as the Reactive Intermediate in the Nitration of Dimethoxybenzenes and Biphenyls.

The pair of isomeric 1,2- and 1,3-dimethoxybenzenes in Table IV reacted readily with 1.5 equiv. of nitrogen dioxide in dichloromethane under the same anaerobic conditions as that described for *p*-dimethoxybenzene **Ia** (Table I). While 1,2-dimethoxybenzene (**IIIa**) gave 3,4-dimethoxynitrobenzene in quantitative

Table IV. Polymethoxybenzenes and Diphenyls in Series **III** as Electron Donors[a]

	Donor	$E_{1/2}$	Product (%)	
IIIa.		1.399		(100)
IIIb.		(1.476)	—[b]	
IIIc.		0.960		(100)
IIId.		1.361		(15)
				(85)
IIIe.		1.476		(100)

[a]As in Tables I and II. [b]See text.

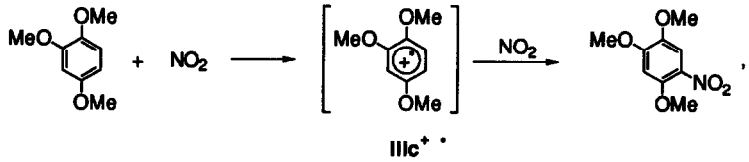
yield, the behavior of the meta isomer **IIIb** was more complex. Immediately upon mixing 1,3-dimethoxybenzene and nitrogen dioxide, the dichloromethane solution turned blue, suggestive of the presence of the distonic (radical-cation) adduct, i.e.[22, 23]

(16)

Consistent with this formulation was the recovery of *m*-dimethoxybenzene largely intact[22] when the reaction mixture was quenched with water. GC-MS analysis of the crude extract indicated the presence of small amounts of bi- and triaryls,[24] together with traces of nitrated and nitrosated products.

The better donor 1,2,4-trimethoxybenzene (**IIIc**) was rapidly converted to 2,4,5-trimethoxynitrobenzene in quantitative yield on treatment with 1.5 equiv. of nitrogen dioxide in cold dichloromethane solution. However, the reaction was noteworthy in that immediately on mixing the prechilled solutions of **IIIc** and nitrogen dioxide at -78 °C, a fleeting green color was observed. The absorption spectrum in Figure 1 shows the green color to be associated with a transient species with λ_{max} = 605 nm (sh 570 nm) and a long low-energy

tail extending beyond 700 nm. It was readily assigned to 1,2,4-trimethoxybenzene cation radical (**IIIc**$^{+\cdot}$) by spectral comparison with an authentic specimen[25] shown in the inset of Figure 1. The green color rapidly faded to a pale yellow solution from which 2,4,5-trimethylnitrobenzene was isolated in quantitative yield upon removal of the solvent (and nitric oxide) *in vacuo*.



IIIc$^{+\cdot}$ (17)

The reaction was repeated with excess trimethoxybenzene (10 equiv.) in dichloromethane at -78 °C, by adding a solution of nitrogen dioxide (1 equiv.) in dichloromethane over the course of < 1 min. The characteristic green color of **IIIc**$^{+\cdot}$ was apparent throughout the addition, and became progressively more intense with incremental additions. The green solution was transformed to a brown color upon continued stirring at -78 °C for 2 h. After

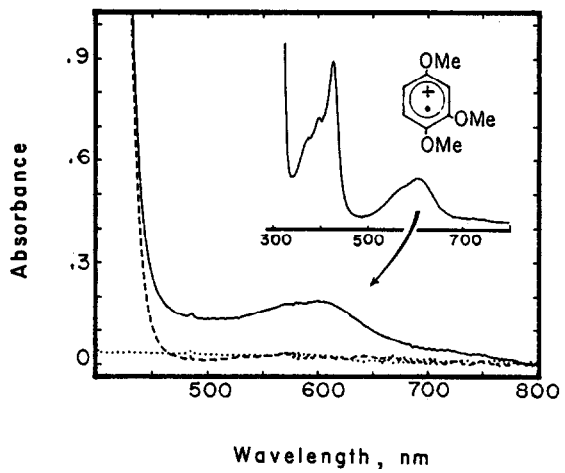
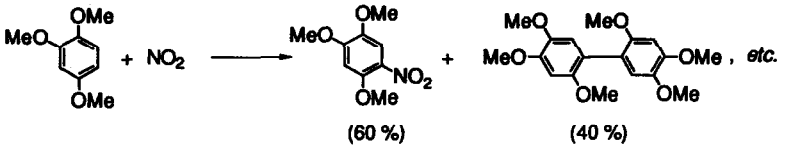


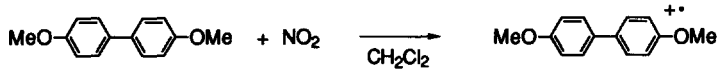
Figure 1. Absorption spectrum of 0.08 M 1,2,4-trimethoxybenzene (**IIIc**) and 0.006 M nitrogen dioxide in dichloromethane immediately upon mixing (———) and after 5 min (------). Spectrum of 0.006 M nitrogen dioxide alone (.....) in dichloromethane. Inset: Absorption spectrum of 1,2,4-trimethoxybenzene cation radical (**IIIc**$^{+\cdot}$) in dichloromethane.

removal of the solvent *in vacuo*, the residue was found to contain roughly equal amounts of 2,4,5-trimethoxynitrobenzene and the dimeric hexamethoxybiphenyl,[26] i.e.



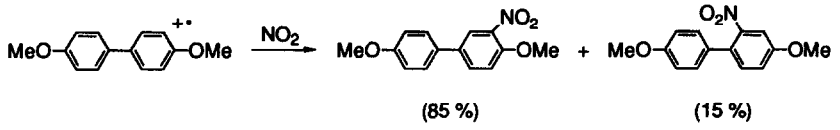
(18)

Transient radical cations were also observed as kinetic intermediate when 4,4'-dimethoxybiphenyl (**IIId**) and its 2,2',6,6'-tetramethyl analogue (**IIIe**) were treated with nitrogen dioxide in dichloromethane. The absorption spectrum of the green transient from *p*-dimethoxybiphenyl corresponds to that of the radical cation (**IIId**$^{+\cdot}$) with λ_{max} = 730, 815 nm,[27] i.e.



(19)

Workup of the reaction mixture quantitatively yielded the pair of isomeric products 2-nitro and 3-nitro-4,4'-dimethoxybiphenyl.

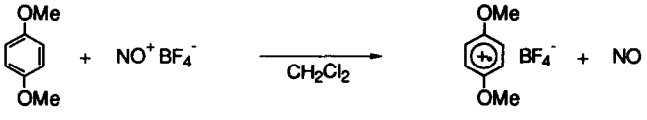


(20)

A similar green transient of the cation radical (**IIIe**$^{+\cdot}$) was also readily observed during the nitration of 2,2',6,6'-tetramethyl-4,4'-dimethoxybiphenyl with nitrogen dioxide to yield the single 3-nitro product in quantitative yield.[28]

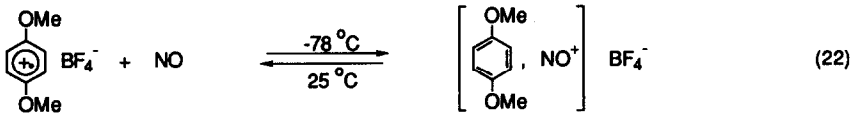
VII. Formation and Reaction of Dimethoxybenzene Radical Cations with Nitrogen Oxides.

The radical cation of the parent *p*-dimethoxybenzene (**Ia**) was generated as a relatively persistent species by direct oxidation with nitrosonium tetrafluoroborate. Thus the addition of NO^+ BF_4^- to a colorless solution of 1,4-dimethoxybenzene in dichloromethane followed by vigorous stirring of the heterogeneous mixture under an argon atmosphere at 25 °C resulted in the dissolution of nitrosonium salt and the formation of a canary yellow-colored solution. UV-vis spectral analysis of the yellow solution revealed an absorption band with a characteristic double maximum at 433 and 460 nm of the *p*-dimethoxybenzene cation radical,[29] shown in Figure 2 (inset). Furthermore, UV-vis and IR spectral analysis of the head gas clearly indicated that nitric oxide was formed according to eq 21.



(21)

Addition of Nitric Oxide. The solution of the radical cation $\mathbf{Ia}^{+\cdot}$ generated at 25 °C by nitrosonium in eq 21 was placed under an atmosphere of nitric oxide. The intensity of the UV-vis absorption band attributed to the cation radical showed no change, and the cation radical was clearly stable for prolonged periods in the presence of excess nitric oxide. Interestingly, the canary yellow solution bleached when it was cooled to -78 °C. Conversely, the color reappeared with its original intensity when the solution was warmed to 25 °C. The quantitative effects of this dramatic color change (which was completely reversible over multiple cooling / warming cycles) is illustrated in Figure 2. The concomitant appearance of a new absorption band with λ_{max} = 366 nm was associated with [**Ia**, NO^+] as the charge-transfer complex of the type previously delineated in detail.[30] The single isosbestic point thus confirmed the temperature-dependent (reversible) electron transfer in eq 22.



(22)

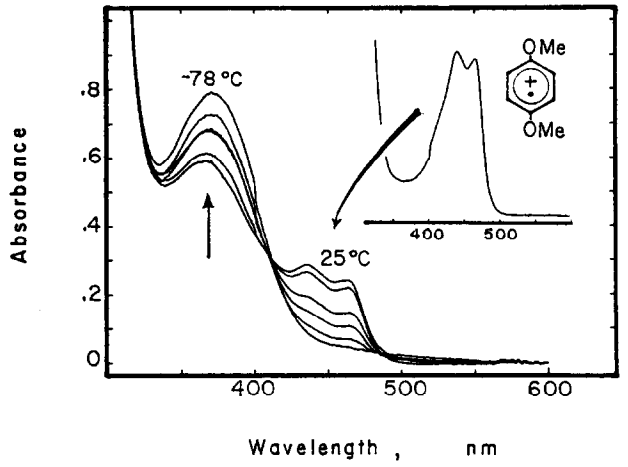


Figure 2. Temperture-dependent spectral change of 0.1 M *p*-dimethoxy-benzene (**Ia**) and 0.1 M NO^+ BF_4^- on mixing at -78 °C and upon incrementally raising the temperature to 25 °C. Inset: Absorption spectrum of *p*-dimethoxy-benzene cation radical ($\mathbf{Ia}^{+\cdot}$) in dichloromethane.

Reaction with Nitrogen Dioxide. Dimethoxybenzene radical cation (**Ia**$^{+\cdot}$) free of nitric oxide was produced from eq 21 by entrainment of the solution with a stream of O_2-free argon. The resultant yellow solution containing only **Ia**$^{+\cdot}$ BF_4^- was cooled to -78 °C, and a precooled solution of nitrogen dioxide in dichloromethane was added dropwise. Immediate workup of the reaction mixture led to 2,5-dimethoxynitrobenzene in close to quantitative yield (see Experimental Section), i.e.

(23)

In an alternative experiment, nitrogen dioxide was directly generated from eq 21 by rapid autoxidation of nitric oxide *in situ*.[12] [The formation of nitrogen dioxide was visually apparent by the appearance of its characteristic brown color in the head gas upon the introduction of dioxygen.] Dimethoxybenzene radical cation was rapidly consumed, and the solvent was then removed *in vacuo*. The crude yellow solid (analyzed by NMR and GC-MS) was pure 2,5-dimethoxynitrobenzene.

Discussion

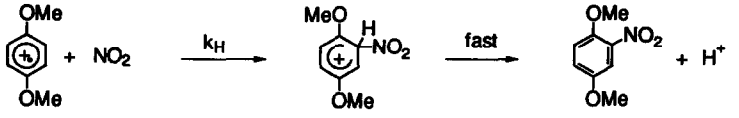
The dialkyl ethers of various hydroquinones in series **I**, **II** and **III** are all effective electron donors by virtue of their reversible oxidation potentials with $E_{1/2} < 1.5$ V vs SCE, as listed in Table I, II and IV. By contrast, the corresponding di-acetates are significantly weaker donors by roughly 12 kcal mol^{-1} (Table II, entries 8 and 12). Consistent with this discrepency, all the dialkoxybenzenes react readily with nitrogen dioxide in dichloromethane solutions (even at -30 °C), whereas diacetoxybenzenes are singularly inert under these conditions.

Among different aromatic donors, the chemical behavior of dialkoxybenzenes toward nitrogen dioxide is unique in that two quite distinctive types of products are derived under identical reaction conditions. Thus the dimethoxybenzenes **Ia**, **Ib**, **Ic** and **Ie** and the dialkoxybenzenes in series **II** consistently undergo ring nitration (eq 3) at fast rates to produce nitroarenes in essentially quantitative yields (see Table I and II). On the other hand, other dimethoxybenzenes (such as **Id**, **If** and **Ig**) react with nitrogen dioxide at the same fast rates to produce the corresponding *p*-benzoquinones via oxidative demethylation (eq 5). With certain dimethoxybenzenes (**Id** and **IV**) ring nitration and oxidative demethylation are simultaneously effected by clearly competitive processes (eq 8). Indeed the intra- and intermolecular competitions described in eqs 9 and 10, respectively, clearly establish ring nitration / oxidative demethylation to proceed at comparable rates. Therefore any mechanistic formulation must perforce take explicit account of these coincident processes.

I. Aromatic Radical Cations as the Reactive Intermediates in Nitration

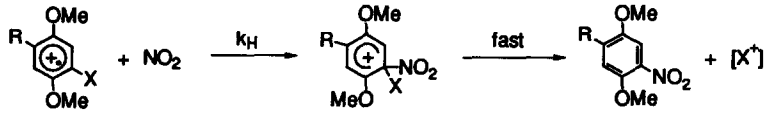
The spectral observation of the aromatic radical cation as the reactive intermediate in Figure 1, we believe, represents the key to understanding how the various dialkoxybenzenes are simultaneously nitrated and demethylated by nitrogen dioxide. The intermediacy of aromatic radical cations is also supported by the isolation of unusual coupled byproducts such as dimeric biaryls in eqs 16 and 18.[32] The most direct pathway by which

the aromatic radical cation leads to ring nitration involves its facile homolytic coupling (k_H) with nitrogen dioxide.[34] The subsequent deprotonation of the Wheland intermediate is known to be rapid,[35] e.g.



(24)

Homolytic coupling is also responsible for the nitro-dealkylations in eqs 12-15 when it occurs at an ipso position of the aromatic cation radical, i.e.



(25)

where X = *tert*-butyl, methoxymethyl, butoxymethyl, etc. that produce relatively stabilized cations.[36]

Homolytic coupling of the dialkoxybenzene radical cation with nitrogen dioxide is regiospecific to form the products in eqs 24 and 25. Thus the mono-alkyl derivative **Ib** leads to a single isomer resulting from para-nitration to the methyl group. The same selectivity extends to the dimethyl derivatives **Ic** and **Ie**. On the other hand, the 2,5-isomer **Id** (with no free para position) is not nitrated, but suffers oxidative dealkylation. Other 2,5-dialkyl compounds (with R = methoxymethyl, *t*-butyl, butoxymethyl, etc., that are susceptible to cationic cleavage) undergo nitro-dealkylation via the cationic ipso adduct (eq 25) that is likely to be in reversible equilibrium with the other (ipso) isomers. Finally, the radical cations of the 2,3,5-trialkyl (derivatives **If**, **IV** and **IVa** undergo a homolytic coupling with nitrogen dioxide that is competitive with the reaction leading to oxidative dealkylation (see eq 9).

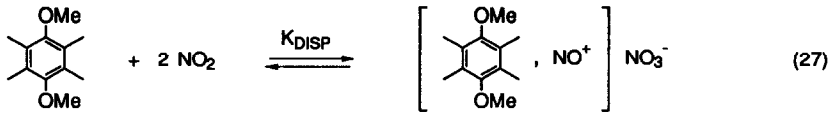
II. Formation of Aromatic Radical Cations via Electron Transfer with Nitrosonium

Independent experiments described in eq 21 establish the rapidity with which dialkoxybenzene donors are oxidized by nitrosonium, as a 1-electron oxidant, [30, 31] i.e.

(26)

Since the oxidation potential of *p*-dimethoxybenzene with $E_{1/2}$ = 1.40 V is (roughly) comparable to the potential ($E_{1/2}$ = 1.50 V) at which nitrosonium is reduced to nitric oxide,[37] the driving force for electron transfer in eq 26 is slightly exergonic.

As applied to nitrogen dioxide pertinent to this study, the nitrosonium oxidant is spontaneously generated during the arene-induced disproportionation of nitrogen dioxide according to eq 1, i.e.[7]



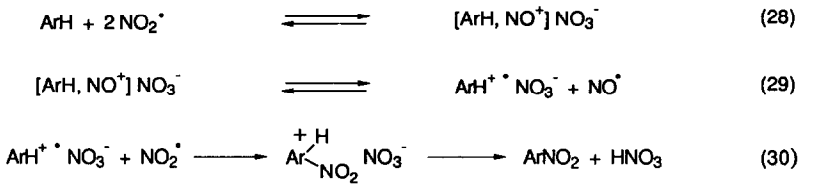
(27)

Such a disproportionation of nitrogen dioxide is expected to be more important than that originally observed with hexamethylbenzene[7] owing to values of $E_{1/2}$ of dialkoxybenzenes which are generally more negative than those of the (poly)methylbenzenes.[8]

III. Mechanism of Aromatic Nitration With Nitrogen Dioxide

Disproportionation (eq 27) and homolytic coupling (eq 24) constitute the principal steps in the formation and reaction of aromatic radical cations, respectively, from nitrogen dioxide. Accordingly, the general mechanism of aromatic nitration with nitrogen dioxide can be readily formulated as

Scheme I

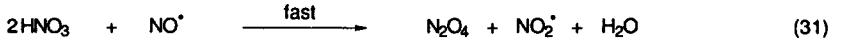


(28)

(29)

(30)

Finally, the rapid reductive dehydration of the nitric acid formed in eq 30 by nitric oxide,[38] i.e.



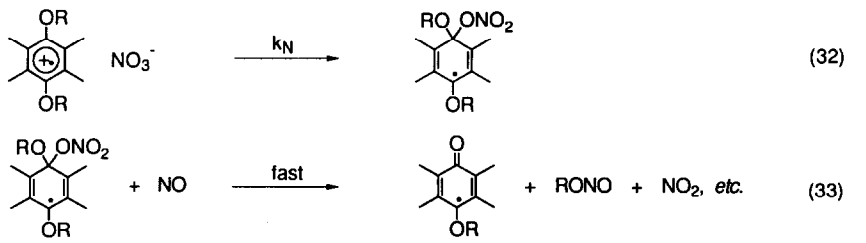
(31)

completes the experimental stoichiometry for aromatic nitration that is observed in eq 1.

IV. Dealkylation of Dialkoxybenzene Cation Radicals by Nitrate.

The formation of radical cations in eq 29 also provides a pathway for oxidative dealkylation of dialkoxybenzenes. Thus the facile loss of the alkoxy group from the radical cation was recently shown[5] to occur by rapid quenching with nitrate -- most likely via the nucleophilic collapse (k_N) at the ipso position, i.e.[39]

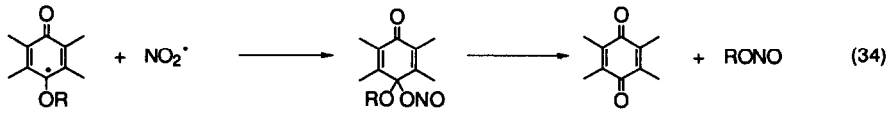
Scheme II



(32)

(33)

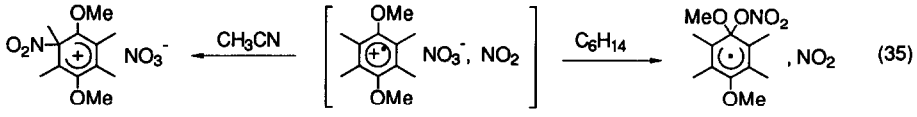
The loss of the second alkoxy group proceeds from the alkyl semi-quinone radical in eq 33 via an analogous series of fast homolytic reactions, e.g.



(34)

V. Aromatic Nitration *versus* Oxidative Dealkylation as a Distinction between Radical-Pair [$ArH^{+}\cdot$, NO_2] and Ion-Pair [$ArH^{+}\cdot$, NO_3^{-}] Annihilation

According to Schemes I and II, the competition between ring nitration and oxidative dealkylation is determined by the relative rates by which the radical cation reacts with nitrogen dioxide and nitrate in eqs 30 and 32, respectively. Significantly, these two rate processes represent distinguishable charge types -- the homolytic coupling (k_H) is a cation / neutral or *radical-pair* annihilation, whereas the nucleophilic attack (k_N) is a cation / anion or *ion-pair* annihilation. As such, the competition should be modulated by the polarity of the solvent.[40] Indeed, the experimental results in Table III provide strong support for such a mechanistic dichotomy. Thus the *intra*molecular competition in the dialkoxybenzene IV favors oxidative dealkylation via *ion-pair* collapse in the nonpolar solvent (entry 1), but it favors nitration via *radical-pair* annihilation in the polar solvent (entry 4), i.e.



(35)

This formulation also receives strong support from the competition between aromatic nitration and oxidative dealkylation which is modulated by added nitrate salt. Thus the presence of extra nitrate is sufficient to alter the predominant nitration of the dialkoxybenzene **IV** in acetonitrile to predominant dealkylation (Table III, entry 6).

The effect of solvent polarity extends to the intramolecular competition between nitro-dealkylation and oxidative dealkylation in eq 15 since it also depends on the differentiation between radical-pair (eq 25) and ion-pair annihilation (eq 32), respectively. Moreover, the same distinction applies to the *inter*molecular competition in eqs 10 and 11, which is particularly noteworthy in that the solvent effect on the competition is not strongly dependent on the donor strength of the dialkoxybenzene.[41] It is important to note that the homolytic coupling of $ArH^{+}\cdot$ and $NO_2\cdot$ is subject to second-order kinetics, while nucleophilic attack is a first-order process that proceeds via the predominant ion-pair [$ArH^{+}\cdot$, NO_3^{-}] in non polar solvents.[42] Optimum conditions for aromatic nitration thus call for high concentrations of nitrogen dioxide in polar solvents, in which ion pairs are less prevalent.[43]

Experimental

Materials

Nitrogen dioxide (Aldrich) was collected in a cold trap at -78 °C as a blue solid of dinitrogen tetroxide contaminated with dinitrogen trioxide. The latter was removed by warming the solid to -5 °C and bubbling in dry oxygen until the liquid became colorless upon refreezing. The excess oxygen was removed *in vacuo* and the dinitrogen tetroxide distilled from phosphorous pentoxide.[44] Solutions of nitrogen dioxide in anhydrous dichloromethane were prepared volumetrically, and stored in a Schlenk tube (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. Bis-(triphenylphosphoranylidene)-ammonium nitrate, $PPN^+ NO_3^-$, was prepared according to Ruff and Schlientz's procedure.[45] Tetra-*n*-butylammonium 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 bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk tube 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 the liquid was colorless. The MnO_2 was removed by filtration. The acetonitrile was first distilled from P_2O_5 under an argon atmosphere and then refluxed over CaH_2 for 6 h. After distillation from the CaH_2, the solvent was stored in a Schlenk flask under an argon atmosphere. The aromatic hydrocarbons 1,4-dimethoxybenzene (**Ia**), 1,2-dimethoxybenzene (**IIIa**), 1,3-dimethoxybenzene (**IIIb**), 1,2,4-trimethoxybenzene (**IIIc**), 4,4'-dimethoxybiphenyl (**IIId**), *p*-hydroquinone, 2-methyl-*p*-hydroquinone, 2,3-dimethyl-*p*-hydroquinone, 2,6-di-*tert*-butyl-*p*-hydroquinone, 2,5-di-*tert*-butyl-*p*-hydroquinone, 2,3,5-trimethyl-*p*-hydroquinone, 1,4-diacetoxybenzene (**IIh**) and 4-methoxyphenol (Aldrich) were used as received. 2'-(4-Methoxyphenoxy)ethylacetate (**IIe**),[46] ethyl (4-methoxyphenoxy)acetate (**IIf**),[46] 2'-(4-methoxyphenoxy)ethanol (**IIg**),[46] 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene,[5] 1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthraquinone,[5] 1,4-dimethoxydurene (**1g**)[5] and 5,8-diacetoxy-1,4-methano-1,2,3,4,-tetrahydronaphthalene (**IIm**)[47] were available from literature procedures. The dialkoxybenzenes used in this study were prepared by alkylation of readily available hydroquinones using common procedures.[48] Characteristic spectral data are given below:

2-Methyl-1,4-dimethoxybenzene (**Ib**): ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3), 3.80 (s, 3), 3.83 (s, 3), 6.8 (m, 3); ^{13}C NMR ($CDCl_3$) δ 16.16, 55.32, 55.56, 110.56, 110.70, 116.91, 127.58, 151.94, 153.29; *m/z* 152 (M^+). *2,3-Dimethyl-1,4-dimethoxybenzene* (**Ic**): ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 6), 3.78 (s, 6), 6.66 (s, 2); ^{13}C NMR ($CDCl_3$) δ 12.02, 56.00, 107.72, 126.64, 151.84; *m/z* 166 (M^+). *2,5-Dimethyl-1,4-dimethoxybenzene* (**Id**): ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6), 3.80 (s, 6), 6.68 (s, 2); ^{13}C NMR ($CDCl_3$) δ 16.04, 55.98, 113.56, 124.13, 151.31; *m/z* 166 (M^+). *2,6-Dimethyl-1,4-dimethoxybenzene* (**Ie**): ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 6), 3.65 (s, 3), 3.71 (s, 3), 6.53 (s, 2); ^{13}C NMR ($CDCl_3$) δ 16.10, 55.09, 59.66, 113.44, 131.397, 150.59, 155.14 ; *m/z* 166 (M^+) *2,3,5-Trimethyl-1,4-dimethoxybenzene* (**If**): ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3), 2.20 (s, 3), 2.28 (s, 3), 3.65 (s, 3), 3.77 (s, 3), 6.53 (s, 1); ^{13}C NMR ($CDCl_3$) δ 11.84, 12.61, 16.27, 55.76, 60.11, 110, 127.66, 130.57, 150.49, 153.32; *m/z* 180 (M^+). *1,4-Di-iso-propoxybenzene* (**IIb**): ^{1}H NMR ($CDCl_3$) δ 1.30 (d, J = 6.3, 12), 5.44 (septet, J = 6.3, 2) 6.82 (s, 4); ^{13}C NMR ($CDCl_3$) δ 22.43, 70.98, 117.56, 152.20; *m/z* 194

(M^+). *1,4-Diallyloxybenzene* (**IIc**): ^1H NMR ($CDCl_3$) δ 4.48 (dt, J = 5.1, 1.5, 4), 5.28 (dd, J = 10.5, 1.2, 2), 5.41 (dd, J = 18, 1.2, 2), 6.05 (m, J = 5.4, 2), 6.86 (s, 4); ^{13}C NMR ($CDCl_3$) δ 69.24, 115.46, 117.28, 133.47, 152.71; *m/z* 190 (M^+). *4-Octyloxyanisole* (**IId**): ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 6.3, 3), 1.32 (m, 10), 1.47 (m, 2), 1.80 (m, 2), 3.76 (s, 3), 3.91 (t, J = 6.6, 2), 6.84 (s, 4); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.62, 26.02, 29.35, 29.22, 31.78, 55.52, 68.50, 114.47, 115.28, 153.22, 153.56; *m/z* 236 (M^+). *5,8-Dimethoxy-1,4-methano-1,2,3,4-tetrahydronapthalene* (**IIi**): ^1H NMR ($CDCl_3$) δ 1.25 (m, 2), 1.53 (m, 1), 1.76 (m, 1), 1.96 (m, 2), 3.67 (s, 2), 3.85 (s, 6), 6.65 (s, 2); ^{13}C NMR ($CDCl_3$) δ 26.33, 39.98, 48.94, 55.84, 109.02, 136.84, 147.57; *m/z* 204 (M^+). *5,8-Dimethoxy-1,4-ethano-1,4-dihydronapthalene* (**IIj**): ^1H NMR ($CDCl_3$) δ 1.43-1.61 (m, 4), 3.84 (s, 6), 4.50 (m, 2), 6.57 (m, 2), 6.65 (s, 2); ^{13}C NMR ($CDCl_3$) δ 24.95, 32.99, 55.95, 107.60, 133.88, 135.16, 147.93; *m/z* 216 (M^+). *5,8-Dimethoxy-1,4-ethano-1,2,3,4-tetrahydronapthalene* (**IIk**): ^1H NMR ($CDCl_3$) δ 1.38 (m, 4), 1.79 (m, 4), 3.53 (s, 2), 3.84 (s, 6), 6.73 (s, 2); ^{13}C NMR ($CDCl_3$) δ 25.52, 26.11, 56.08, 107.94, 133.53, 148.45; *m/z* 218 (M^+). *2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl* (**IIIe**)[49]: ^1H NMR ($CDCl_3$) δ 2.33 (s, 12), 3.74 (s, 6), 7.18 (s, 4); ^{13}C NMR ($CDCl_3$) δ 16.21, 59.74, 127.36, 130.89, 136.51, 156.18; *m/z* 270 (M^+). *5,8-Dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene* (**IV**): ^1H NMR ($CDCl_3$) δ 1.23 (m, 2), 1.50 (m, 1), 1.71 (m, 1), 1.92 (m, 2), 2.26 (s, 3), 3.59 (m, 2), 3.80 (s, 3), 3.78 (s, 3), 6.48 (s, 1); ^{13}C NMR ($CDCl_3$) δ 16.03, 26.48, 26.90, 39.57, 40.83, 48.84, 55.57, 60.59, 110.99, 128.03, 134.06, 140.34, 146.06, 148.67; *m/z* 218 (M^+). *2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl*[50]: ^1H NMR ($CDCl_3$) δ 2.04 (s, 6), 2.19 (s, 6), 3.83 (s, 6), 6.70 (s, 2), 6.86 (s, 2); ^{13}C NMR ($CDCl_3$) δ 15.43, 19.64, 59.94, 110.90, 122.95, 131.76, 132.98, 134.11, 156.17; *m/z* 270 (M^+). *2,5-Dimethoxymethyl-1,4-dimethoxybenzene*[51]: *General Procedure:* A solution of 2,5-dichloromethyl-1,4-dimethoxybenzene[52] (20 mmol) in methanol (20 mL) was added to a freshly prepared solution of sodium methoxide (2.3 g Na in 50 mL methanol). The mixture was refluxed for 2 h, cooled to 25 °C, diluted with water and extracted with ether (3 x 50 mL). The solvent was evaporated and the solid recrystallized from methanol / water. mp. 57-58 °C (lit[51] mp 56-59 °C); ^1H NMR ($CDCl_3$) δ 3.39 (s, 6), 3.77 (s, 6), 4.46 (s, 4), 6.90 (s, 2); ^{13}C NMR ($CDCl_3$) δ 55.84, 58.19, 69.11, 111.16, 126.10, 150.73; *m/z* 226 (M^+). The other methoxymethylarenes were prepared similarly from the corresponding chloromethylarenes. *5,8-Dimethoxy-6-methoxymethyl-7-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene* (**IVa**): ^1H NMR ($CDCl_3$) δ 1.23 (sym m, 2), 1.46 (sym m, 1), 1.67 (sym m, 1), 1.92 (sym m, 2), 2.25 (s, 3), 3.40 (s, 3), 3.57 (br s, 2), 3.74 (s, 3), 3.80 (s, 3), 4.43 (AB pattern, $\Delta\nu_{AB}$ = 21.06 Hz, J_{AB} = 9.9 Hz, 2H, $-CH_2-$ of methoxymethyl group) ; ^{13}C NMR ($CDCl_3$) δ 11.52, 26.84, 40.55, 40.60, 48.60, 58.05, 60.60, 61.80, 66.29, 126.77, 129.16, 137.36, 140.59, 148.00, 148.57; m/z 262 (M^+). *2-Methoxymethyl-3,4,5-trimethyl-1,4-dimethoxybenzene* (**V**): mp 34-36 °C; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3), 2.19 (s, 3), 2.30 (s, 3), 3.42 (s, 3), 3.64 (s, 3), 3.69 (s, 3), 4.47 (s, 2); ^{13}C NMR ($CDCl_3$) δ 11.63, 12.42, 12.71, 58.05, 59.88, 61.73, 66.69, 127.31, 127.83, 129.12, 130.91, 152.94, 153.50; *m/z* 224 (M^+). *2-Methoxymethyl-1,4-dimethoxybenzene:* ^1H NMR ($CDCl_3$) δ 3.39 (s, 3), 3.72 (s, 6), 4.45 (s, 2), 6.74 (s, 2), 6.95 (s, 1); ^{13}C NMR ($CDCl_3$) δ 55.18, 55.46, 57.97, 69.02, 110.84, 112.61, 114.17, 127.34, 150.82, 153.27; *m/z* 182 (M^+). *2,5-Di-n-butoxymethyl-1,4-dimethoxybenzene:* mp 31-32 °C; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.2, 6), 1.41 (m, 4), 1.62 (m, 4), 3.51 (t, J = 6.6, 4), 3.80 (s, 6), 4.53 (s, 4), 6.96 (s, 2); ^{13}C NMR ($CDCl_3$) δ 13.91, 19.36, 31.81, 55.98, 67.17, 70.34, 111.17, 126.58, 150.83; *m/z* 310 (M^+). *2,5-Di-tert-butyl-1,4-dimethoxybenzene:* ^1H NMR ($CDCl_3$) δ 1.37 (s, 18), 3.80 (s, 6), 6.83 (s, 2); ^{13}C NMR ($CDCl_3$) δ 29.78, 34.58, 55.85, 111.60, 136.25, 151.93; m/z 250 (M^+). *2,6-Di-tert-*

butyl-1,4-dimethoxybenzene: ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 18), 3.71 (s, 3), 3.82 (s, 3), 6.85 (s, 2); ^{13}C NMR ($CDCl_3$) δ 31.98, 35.90, 55.09, 64.17, 111.65, 144.36, 143.86, 153.23, 154.24; *m/z* 250 (M^+).

Instrumentation

The UV-vis absorption spectra were recorded on a Hewlett-Packard 8450A diode array spectrometer. IR spectra were recorded on a Nicolet 10DX FT spectrometer. Gas phase IR spectra were recorded with a 5-cm path-length cell. The ^{1}H 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 Dialkoxybenzenes.

Cyclic voltammetry (CV) was performed on a BAS 100A Electrochemical Analyzer. The CV cell was of an airtight design with high vacuum 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 embeded 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 was 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 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) and 5 x 10^{-3} M dialkoxybenzene in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at the sweep rate of 100 mV s^{-1} and were IR compensated. The potentials were referenced to SCE which was calibrated with added ferrocene (5 x 10^{-3} M). The oxidation potential ($E_{1/2}$) values were calculated by taking the average of the anodic and cathodic peak potentials.

Nitration of the 1,4-Dimethoxybenzenes with Nitrogen Dioxide.

General procedure: A prechilled (-78 °C) dichloromethane solution of nitrogen dioxide (3 mL, 0.2 M, 0.6 mmol) was added to a cold (-78 °C) solution of 1,4-dimethoxybenzene (**Ia**) (55 mg, 0.2 M, 0.4 mmol) under an argon atmosphere. A bright yellow color formed immediately. This color faded slightly within 1 min. The cold reaction mixture was stirred at -78 °C for 2 minutes in the dark. The solution was warmed to room temperature and stirred for 15 min. The side arm of the reaction flask was then connected to an evacuated gas phase IR cell and the head gas sampled. Nitric oxide was identified (as the only nitrogen oxide present) by the characteristic NO stretching frequency[10] at 1876 cm^{-1}. 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 characteristic absorptions at λ_{NO} = 204, 214 and 226 nm of nitric oxide were observed.[11] Addition of air into the cell led to the characteristic brown color of NO_2 which was confirmed by the stretching frequencies at 1629 and 1600 cm^{-1} in the IR spectrum.[53] The solvent and nitrogen oxides were removed *in vacuo*, and quantitative GC and NMR analysis indicated that 2,5-dimethoxynitrobenzene[46] (0.39 mmol) was the only product. The water formed in the reaction was observed on the sides of the flask but not quantified.

The stoichiometry of the reaction was determined by first establishing the required molar ratios of reactants. Thus when a cold (-78 °C) dichloromethane solution of 1,4-dimethoxybenzene (2 mL, 0.2 M, 0.40 mmol) was treated with 2 equiv. of NO_2 (4 mL, 0.2 M, 0.8 mmol), the reaction mixture immediately became yellow but rapidly turned greenish. UV-vis analysis of the cold solution revealed a broad absorption at λ_{max} = 690 nm[54a] indicative of dinitrogen trioxide (formed by complexation of the nitric oxide, produced in the reaction, with the excess unreacted nitrogen dioxide). The solution was then warmed to room temperature and IR analysis of the head gas indicated the absorptions of both NO (1875 cm^{-1})[10] and NO_2 (1600 and 1620 cm^{-1})[53]. [Note that N_2O_3 is largely dissociated, 80 %, at 25 °C].[54] On removal of the solvent and excess nitrogen oxides *in vacuo*, a quantitative yield of 2,5-dimethoxynitrobenzene (0.40 mmol) was obtained. Treatment of 1,4-dimethoxybenzene with less than 1.5 equiv. of nitrogen dioxide led to incomplete reaction and the recovery of a portion of the (unreacted) dimethoxybenzene.

The dialkoxybenzenes listed below were nitrated using the above procedure to afford the corresponding nitroarenes in quantitative yield. The isolated nitroarenes were analyzed by GC-MS, NMR and IR spectroscopy and also by comparision with authentic samples. *2-Methyl-1,4-dimethoxybenzene* (**Ib**): 2,5-Dimethoxy-4-methylnitro-benzene: mp 110-112 °C; IR (KBr) υ_{max} 3078, 2966, 2920, 2845, 1583, 1514 (vs), 1445, 1341, 1284, 1267, 1220, 1036, 869, 794, 759,719 cm-^{1}; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3), 3.34 (s, 3), 3.82 (s, 3), 6.82 (s, 1), 7.27 (s, 1); ^{13}C NMR ($CDCl_3$) δ 16.52, 55.66, 56.68, 106.56, 116.03, 135.13, 136.19, 147.39, 150.58; *m/z* 197 (M^+). *2,3-Dimethyl-1,4-dimethoxybenzene* (**Ic**): 3,4-Dimethyl-2,5-dimethoxynitrobenzene: mp 64-65 °C; IR (KBr) υ_{max} 3005, 2943, 2838, 1518 (vs), 1474, 1351, 1246, 1118, 1090, 1006, 845, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3), 2.24 (s, 3), 3.80 (s, 3), 3.82 (s, 3), 7.18 (s, 1); ^{13}C NMR ($CDCl_3$) δ 12.75, 55.90, 62.09, 103.78, 133.53, 133.86, 141.16, 145.77, 153.15; *m/z* 211 (M^+). *2,5-Dimethyl-1,4-dimethoxybenzene* (**Id**): 2,5-Dimethyl-1,4-benzoquinone[55] was obtained in 89 % yield together with a complex mixture of at least 4 other minor products. UV-vis analysis of the head gas in this reaction showed absorbances at λ_{max} = 319, 328, 339, 351 and 365 nm characteristic of methyl nitrite.[14] 2,5-Dimethyl-1,4-benzoquinone: mp 122-123 °C (lit[55] mp 122.5-123.5 °C); IR (KBr) υ_{max} 3258, 3046, 2961, 2925, 1666 (vs), 1641 (vs), 1439, 1379,1349, 1253, 1155, 1004, 928, 797, 709, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94 (m, 6), 6.52 (m, 2); ^{13}C NMR ($CDCl_3$) δ 15.40, 133.24, 145.67, 187.92; *m/z* 136 (M^+). Two of these products were tentatively identified as (4-methyl-2,5-dimethoxyphenyl)nitromethane: ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3), 3.78 (s, 6), 5.45 (s, 2), 6.77 (s, 2); MS m/z (retention time = 7.19 min.) 211 (4, M^+), 165 (100), 135 (61), 105 (22), 91 (38), and 2,5-dimethoxy-4-methylbenzylnitrate: ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3), 3.77 (s, 6), 5.42 (s, 2), 6.74 (s, 2); GC-MS (retention time = 7.10 min.) *m/z* 228 (2, M^+), 180 (70), 166 (100), 165 (61), 151 (32), 137 (43), 136 (33), 134 (47), 123 (33), 121 (31), 91 (59). *2,6-Dimethyl-1,4-dimethoxybenzene* (**Ie**): 2,4-Dimethyl-3,6-dimethoxynitrobenzene: IR (neat) υ_{max} 3019, 2984, 2950, 2860, 1614, 1535 (vs), 1461, 1410, 1376, 1331, 1240, 1110, 1059, 1002, 855, 787, 736 cm^{-1}; ^{1}H nmr δ ($CDCl_3$) 2.21 (s, 3), 2.32 (s, 3), 3.69 (s, 3), 3.83 (s, 3), 6.69 (s, 1); ^{13}C NMR ($CDCl_3$) δ 10.88, 15.51, 56.36, 60.28, 111.98, 117.92, 124.29, 134.16, 146.52, 149.95; *m/z* 211 (M^+). *2,3,5-Trimethyl-1,4-dimethoxybenzene (If)*: GC-MS and ^{1}H NMR analysis of the crude reaction product indicated that 2,3,5-trimethylbenzoquinone (80 %): mp. 31-32 °C (lit[56] mp 31-32 °C); IR (KBr) υ_{max} 2961, 2925, 2858, 1650 (vs), 1620, 1439, 1379, 1354, 1319, 1264, 1190, 1106, 1034, 993, 911, 884, 810, 797, 698, 676 cm^{-1}; ^{1}H nmr δ ($CDCl_3$) 1.88 (s, 3), 1.90 (s, 3), 1.92 (d, J = 1.5, 3), 6.43 (q, J = 1.5, 1); ^{13}C NMR ($CDCl_3$) δ 11.84, 12.14, 15.67, 132.83, 140.50, 140.66, 145.11, 187.21, 187.59; *m/z* 150

(M^+), was the major product. In addition, 2,4,5-trimethyl-3,6-dimethoxynitrobenzene (6 %); mp 68-70 °C; IR (KBr) υ_{max} 3006, 2946, 2857, 2833, 1529 (vs), 1468, 1402, 1378, 1246, 1090, 1056, 1026, 1378, 1246, 1090, 1056, 1026, 994, 885, 843, 748 cm^{-1}; ^1H nmr δ ($CDCl_3$) 2.15 (s, 3), 2.16 (s, 3), 2.18 (s, 3) 3.64 (s, 3), 3.73 (s, 3); ^{13}C NMR ($CDCl_3$) δ 10.68, 12.58, 12.90, 60.30, 62.50, 120.80, 130.10, 133.79, 144.96, 145.28, 152.55; m/z 225 (M^+) and traces of side chain *nitrated* products of trimethyl-1,4-dimethoxybenzene, tentatively assigned on the basis of GC-MS analysis [m/z 225 (M^+)].

In a separate experiment, cold dichloromethane solutions (both 0.2 M) of the arene (0.2 mmol) and NO_2 (0.35 mmol) were mixed at -78 °C and stirred at this temperature for 20 min. The solvent and nitrogen oxides were removed *in vacuo* whilst warming to 25 °C. The crude residue, analyzed by GC and GC-MS, was found to contain: 2,3,5-trimethyl-1,4-dimethoxybenzene (33 %), 2,3,5-trimethyl-1,4-benzoquinone (8 %) and traces of trimethyl-2,5-dimethoxynitrobenzene. The major product by GC-MS analysis was a compound (est. 41 %): GC-MS: 211, 164, 150, 149, 121, 91. [The M^+ (m/z = 211) corresponds to the loss of a methyl group from **If** and addition of an NO_2 moiety.] The IR spectrum obtained by subtraction of the spectra of the known components (quinone and the corresponding nitrobenzene) revealed an absorption at υ_{max} 1665 cm^{-1}. If, however, the reaction mixture was allowed to stir for a further 0.5 h before evacuation, this intermediate (tentatively assigned as 4-methoxy-4-nitro-2,3,5-trimethylcyclohexadieneone) was transformed to the quinone quantitatively. 1,4-Di-*iso*-propoxybenzene (**IIb**): 2,5-Di-*iso*-Propoxynitrobenzene: IR (neat) υ_{max} 2978, 2937, 1532 (vs), 1497, 1468, 1376, 1353, 1278, 1220, 1140, 1111, 978, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (d, J = 6.6, 6), 1.25 (d, J = 6.3, 6), 4.39 (m, 2), 6.95 (m, 2), 7.20 (m, 1); ^{13}C NMR ($CDCl_3$) δ 21.63, 21.77, 71.01, 73.44, 111.69, 118.70, 122.06, 141.27, 144.95, 151.06; *m/z* 239 (M^+). 1,4-Diallyloxybenzene (**IIc**): 2,5-Diallyloxynitrobenzene: IR (neat) υ_{max} 3087, 2928, 2871, 1648 vw, 1563, 1529 vs, 1495, 1455, 1427, 1353, 1280, 1217, 1155, 1025, 996, 934, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.48 (dm, J = 5.4, 2), 4.57 (dm, J = 5.4, 2), 5.23-5.44 (m, 4), 5.96 (m, 2), 6.98 (d, J = 9.3, 1), 7.05 (dd, J = 9, 3, 1), 7.33 (d, J = 3, 1); ^{13}C NMR ($CDCl_3$) δ 69.50, 70.69, 110.86, 116.72, 118.07, 118.00, 121.27, 132.31, 132.00, 139.80, 146.12, 151.83; *m/z* 235 (M^+). 4-Octyloxyanisole (**IId**): The nitroarenes were isolated in a 3:1 ratio of the 2- and 3-nitroarenes: IR (KBr) υ_{max} 3083, 2927, 2854, 1530 (vs), 1502, 1468, 1351, 1279, 1223, 1151, 1040, 811 cm^{-1}. 4-Octyloxy-2-nitroanisole: ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6, 3), 1.26 (m, 8), 1.42 (m, 2), 1.77 (m, 2), 3.77 (s, 3), 4.00 (t, J = 6.3, 2), 6.98 (d, J = 9, 1), 7.05 (dd, J = 9, 3, 1), 7.32 (d, J = 3, 1); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.60, 25.79, 25.89, 29.07, 29.13, 29.19, 31.75, 55.95, 57.01, 68.96, 70.43, 109.66, 110.59, 116.35, 120.68, 139.85, 146.80, 152.69; *m/z* 281 (M^+) and 4-octyloxy-3-nitroanisole: ^1H nmr δ ($CDCl_3$) 3.88 (s, 3), 3.90 (t, 6.3, 2), 6.99 (d, J = 9.3, 1), 7.07 (dd, J = 9, 3, 1), 7.35 (d, J = 3, 1); ^{13}C NMR ($CDCl_3$) δ 25.89, 57.01, 68.96, 110.59, 115.00, 121.33, 139.85, 146.80, 147.16, 151.33, 152.69; *m/z* 281 (M^+). *2'(4-Methoxyphenoxy)ethylacetate* (**IIe**): The crude residue contained only the isomeric nitroarenes which were identical in all respects to authentic samples prepared by acetylation of the corresponding authentic alcohols[46]. 2'(4-Methoxy-3-nitro-phenoxy)ethylacetate (66 %): ^1H NMR ($CDCl_3$) δ 2.04 (s, 3), 3.75 (s, 3), 4.11 (t, J = 4.8, 2), 4.35 (t, J = 4.8, 2), 6.98 (d, J = 9.6, 1), 7.08 (dd, J = 3.0, 9.6, 1), 7.35 (d, J = 3.0, 1); ^{13}C NMR ($CDCl_3$) δ 20.66, 56.87, 62.41, 66.78, 110.93, 114.93, 121.35, 139.20, 147.52, 151.47, 170.85; *m/z* 255 (M^+) and 2'(4-methoxy-2-nitro-phenoxy)ethylacetate (34 %): ^1H NMR ($CDCl_3$) δ 2.03 (s, 3), 3.75 (s, 3), 4.20 (t, J = 4.8, 2), 4.35 (t, J = 4.8, 2), 6.99 (d, J = 9.6, 1), 7.04 (dd, J = 3.0, 9.0, 1), 7.28 (d, J = 3.0, 1); ^{13}C NMR ($CDCl_3$) δ 20.54, 55.88, 62.26, 68.84, 109.61, 117.69, 120.48, 140.47, 145.77, 153.51, 170.85; *m/z*

255 (M^+). ***Ethyl 4-methoxyphenoxyacetate*** **(IIf)**: The isomeric nitroarenes: ethyl 4-methoxy-3-nitrophenoxyacetate (80 %) and ethyl 4-methoxy-2-nitrophenoxyacetate (20 %) were identical in all respects to authentic samples.[46] ***2'(4-Methoxyphenoxy)ethanol*** **(IIg)**: The crude product which contained isomeric 2'(4-methoxynitrophenoxy)ethylnitrites, in a 3:2 ratio, identified by GC-MS (m/z 242, M^+) and the characteristic broad nmr signal at $\delta = 5.13$ (t, 4.2, 2). The residue was allowed to stand in the air for 1 day at which time the nitrites had decomposed to the corresponding isomeric alcohols: 2'(4-methoxy-3-nitrophenoxy)ethanol (60 %) and 2'(4-methoxy-2-nitrophenoxy)ethanol (40 %) which were identical in all respects to authentic samples.[46] ***5,8-Dimethoxy-1,4-methano-1,2,3,4-tetrahydronapthalene*** **(IIi)**: 5,8-Dimethoxy-6-nitro-1,4-methano-1,2,3,4-tetrahydronapthalene: mp 72-73 °C; IR (KBr) υ_{max} 3001, 2972, 2949, 2879, 1526 (vs), 1485, 1353, 1301, 1226, 1117, 1094, 1053, 1019, 852, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (m, 2), 1.56 (d, J = 9, 1), 1.76 (md, J = 9, 1), 1.99 (m, 2), 3.65 (m, 1), 3.70 (m, 1), 3.86 (s, 3), 3.94 (s, 3), 7.20 (s, 1); ^{13}C NMR ($CDCl_3$) δ 25.64, 26.30, 40.08, 41.08, 48.94, 55.91, 62.29, 105.82, 141.03, 141.87, 143.19, 143.32, 148.50; *m/z* 249 (M^+). ***5,8-Dimethoxy-1,4-ethano-1,4-dihydronaphthalene*** **(IIj)**: 5,8-Dimethoxy-6-nitro-1,4-ethano-1,4-dihydronapthalene: IR (KBr) υ_{max} 3058, 2945, 2871, 2837, 1648 vw, 1586 vw, 1523, 1484, 1461, 1433, 1348, 1308, 1240, 1223, 1098, 1042, 996, 968, 916, 849, 821, 764, 736, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (m, 2), 1.6 (m, 2), 3.87 (s, 3), 3.93 (s, 3), 4.5 (dm, J = 13, 2), 6.52 (m, 2), 7.23 (s, 1); ^{13}C NMR ($CDCl_3$) δ 24.23, 24.64, 33.07, 34.01, 55.72, 62.87, 104.08, 134.47, 139.95, 140.24, 140.68, 142.09, 148.88; *m/z* 261 (M^+). ***5,8-Dimethoxy-1,4-ethano-1,2,3,4-tetrahydronapthalene*** **(IIk)**: 5,8-Dimethoxy-6-nitro-1,4-ethano-1,2,3,4-tetrahydronapthalene: IR (neat) υ_{max} 2960, 2868, 1521 (vs), 1475, 1329, 1311, 1229, 1118, 1099, 1059, 1011, 842, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (sym m, 4H), 1.73 (sym m, 4H), 3.41 (br t, J = 2.4, 1), 3.46 (br t, J = 2.4, 1), 3.80 (s, 3), 3.83 (s, 3), 7.22 (s, 1); ^{13}C NMR ($CDCl_3$) δ 24.72, 25.06, 26.28, 27.44, 55.84, 63.06, 104.12, 140.24, 140.51, 142.46, 147.75, 149.87; *m/z* 263 (M^+). ***1,2-Dimethoxybenzene*** **(IIIa)**: 3,4-Dimethoxynitrobenzene (mp 96-98 °C) identical in all respects to a commercial sample. ***1,3-Dimethoxybenzene*** **(IIIb)**: A blue-green color developed immediately on mixing the cold (-78 °C) solutions of the arene and NO_2. The color persisted for 1 h after warming to 25 °C. The solution was transferred to a quartz cuvette fitted with a Schlenk stopcock under a flow of argon. The UV-vis absorption spectrum thus recorded showed a broad maximum at λ_{max} = 645 nm.[57] After the usual workup, GC-MS analysis of the crude residue indicated unreacted 1,3-dimethoxybenzene, (45 %); and a mixture of products tentatively identified as: 3-methoxy-4-nitrosoanisole, 6 % [*m/z* 167 (M^+)]; 3-methoxy-4-nitroanisole, 6 % [*m/z* 183 (M^+)]; tetramethoxybiphenyl, ~1 % [*m/z* 274 (M^+)]; and a major unidentified high molecular weight product ~42 %[*m/z* 289 (100), 274 (60), 243 (76)]. ***1,2,4-Trimethoxybenzene*** **(IIIc)**: Immediately on mixing cold (-78 °C) dichloromethane solutions of the arene and NO_2 a green color developed. The solution became yellow on warming to 25 °C. The reaction mixture was worked up and analyzed as usual. 2,3,5-Trimethoxynitrobenzene was isolated: mp 87-89 °C; IR (KBr) υ_{max} 3010, 2977, 2950, 2838, 1624, 1591, 1524 (vs), 1340, 1279, 1223, 1034, 1017, 862, 823, 795 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.89 (s, 3H), 3.97 (s, 3H), 3.99 (s, 3H), 6.58 (s, 1H), 7.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 56.24, 56.89, 97.23, 108.63, 130.45, 142.06, 150.19, 154.63; *m/z* 214 (M^+); along with traces of the dimeric biphenyl: *m/z* 334 (M^+). The reaction was repeated in a quartz cuvette fitted with a side arm and Teflon needle valve. The solution of the NO_2 was placed in the side arm and the arene solution in the cuvette. Both solutions were cooled to -78 °C in an acetone / dry-ice bath. The UV-vis absorption

spectrum was recorded at -78 °C. The cold solutions were rapidly mixed and the absorption maximum at λ_{max} = 600 nm of the resultant green solution was attributed to 1,2,4-trimethoxybenzene cation radical (see Figure 1).

In a second experiment 1 mL of a dichloromethane solution of NO_2 (0.2 M) was added dropwise over 3 min. to a stirred solution of 1,2,4-trimethoxybenzene in dichloromethane (10 mmol, 3.5 mL). As the addition progressed, the green color was observed to increase. After the addition was complete, the solution was dark green. The mixture was stirred at -78 °C for a further 1 h. during which the color became brown. The solvent and excess nitrogen oxides were then evaporated *in vacuo*. GC and GC-MS analysis indicated: 2,3,5-trimethoxynitrobenzene (~0.080 mmol); hexamethoxybiphenyl[58] (~0.055 mmol) and unreacted 1,2,4-trimethoxybenzene (~9.8 mmol). *4,4'-Dimethoxybiphenyl* (**IIId**): Immediately on mixing the cold (-78 °C) solutions of the biphenyl and NO_2, a deep purple color developed. This color persisted undiminished at -78 °C for 30 min. However on warming to 0 °C, the purple color color faded and a transient green color was observed. UV-vis spectral analysis of the green transient species revealed the characteristic maxima at 730 and 815 nm of **IIId**$^{+\cdot}$. After stirring at room temperature for 30 min., the usual workup yielded the isomeric nitrobiphenyls in quantitative yield: IR (KBr) υ_{max} 2966, 2938, 2843, 1613, 1530 (s), 1518 (vs), 1491, 1440, 1357, 1285, 1246, 1179, 1045, 1012, 834 cm^{-1}; 2-Nitro-4,4'-dimethoxybiphenyl (85 %): ^{1}H NMR ($CDCl_3$) δ 3.86 (s,3), 3.91 (s, 3), 6.96 (d, J = 8.7, 2), 7.15 (dd, J = 2.7 and 8.7, 1), 7.24 (d, J = 8.7, 2), 7.34 (d, J = 3.6, 1), 7.36 (d, J = 2.1, 1); ^{13}C NMR ($CDCl_3$) δ 55.25, 55.86, 108.87, 114.09, 114.46, 118.55, 127.75, 129.15, 129.41, 132.72, 158.77, 159.34. 3-Nitro-4,4'-dimethoxybiphenyl (15 %): ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3), 4.01 (s, 3), 7.02 (d, J = 9, 2), 7.51 (d, J = 8.7, 2), 7.75 (dd, J = 2.7, 11.4, 1), 8.06 (d, J = 2.4, 1); ^{13}C NMR ($CDCl_3$) δ 53.40, 60.00, 114.27, 114.43, 123.48, 128.17, 131.97 (quarternary carbons are not recorded due to the small signals). *2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl* (**IIIe**): 2,2',6,6'-Tetramethyl-3-nitro-4,4'-dimethoxy-biphenyl: mp 125-127 °C; IR (KBr) υ_{max} 2949, 2863, 2828, 1526 (vs), 1468, 1411, 1359, 1267, 1220, 1180, 1128, 1048, 1007, 875, 806, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3), 2.34 (s, 6), 2.39 (s, 3), 3.79 (s, 3), 3.82 (s, 3), 7.01 (s, 2), 7.10 (s, 1); ^{13}C NMR ($CDCl_3$) δ 11.00, 59.54, 60.09, 123.00, 128.30, 129.37, 130.60, 131.01, 132.01, 133.36, 149.59, 155.96, 156.93; *m/z* 315 (M^+). *2,2',5,5'-Tetramethyl-4,4'-di-methoxybiphenyl.* In this reaction neither the corresponding quinone nor the nitroaromatic was formed. *5,8-Dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene* (**IV**): The reaction gave a mixture of 1,4-methano-6-methyl-1,2,3,4-tetrahydronaptha-5,8-quinone, (69 %); IR (KBr) υ_{max} 2955, 2880, 1653 (vs), 1589, 1566, 1451, 1376, 1341, 1272, 1174, 1013, 921, 886 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (d, J = 7.5, 2), 1.32 (d, J = 8.7, 1), 1.55 (d, J = 9, 1), 1.84 (d, J = 8.4, 2), 1.94 (s, 3), 3.38 (d, J = 6.3, 2), 6.33 (s, 1); ^{13}C NMR ($CDCl_3$) δ 15.35, 24.74, 40.29, 40.44, 47.48, 132.40, 145.27, 151.34, 184.48, 184.60; GC-MS: *m/z* 188 (M^+) and 5,8-dimethoxy-7-methyl-1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene (20 %); IR (KBr) υ_{max} 2947, 2875, 2835, 1533, 1474, 1370, 1344, 1304, 1226, 1213, 1069, 1010, 984, 951, 877, 787, 722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (sym m, 2), 1.50 (sym m, 1), 1.69 (sym m, 1), 1.96 (sym m, 2), 2.10 (s, 3), 3.59 (br s, 1), 3.62 (br s, 1), 3.75 (s, 3), 3.84 (s, 3); ^{13}C NMR ($CDCl_3$) δ 10.68, 26.51, 40.63, 41.16, 48.65, 61.00, 62.02, 121.19, 137.96, 140.79, 142.58, 143.74, 147.16; GC-MS: *m/z* 263 (M^+). A small amount of unreacted arene (8%) was also detected. *5,8-Dimethoxy-6-methoxy-methyl-7-methyl-1,4-methano-1,2,3,4-tetrahydro-napthalene* (**IVa**): The reaction gave a mixture of 1,4-methano-6-methoxymethyl-7-methyl-1,2,3,4-tetrahydronaptha-5,8-quinone (25 %); IR (neat) υ_{max} 2953, 2927, 2875, 2822, 1645, 1599, 1448, 1376, 1331, 1291, 1272, 1226, 1193, 1102, 997, 951, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (sym m, 2), 1.22

(sym m, 1), 1.43 (sym m, 1), 1.73 (sym m, 2), 1.92 (s, 3), 3.21 (s, 3), 3.30 (br s, 2), 4.13 (AB pattern, $\Delta\nu_{AB}$ = 17.1 Hz, J_{AB} = 10.5 Hz, 2H, -CH_2- of methoxy methyl group); ^{13}C NMR ($CDCl_3$) δ 11.70, 24.71, 40.43, 47.14, 58.44, 64.00, 137.42, 144.01, 150.76, 150.84, 183.14, 184.31; GC-MS: *m/z* 232 (M^+) and 5,8-dimethoxy-7-methyl-1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene (75 %). [Note that nitroarene obtained in this reaction was the same as that produced by the reaction of IV with nitrogen dioxide.] *2-Methoxymethyl-1,4-dimethoxybenzene*: 4-Methoxymethyl-2,5-di-methoxynitrobenzene: mp 84-85 °C; IR (KBr) υ_{max} 2932, 2857, 2828, 1514 (vs), 1468, 1376, 1347, 1284, 1220, 1123, 1030, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.43 (s, 3), 3.78 (s, 3), 3.89 (s, 3), 4.54 (s, 2), 7.15 (s, 1), 7.33 (s, 1); ^{13}C nmr ($CDCl_3$) 55.88, 56.90, 58.73, 68.56, 106.98, 113.09, 134.70, 134.70, 147.74, 149.27; *m/z* 227 (M^+). *2,5-Dimethoxymethyl-1,4-dimethoxybenzene*: 4-Methoxymethyl-2,5-dimethoxynitrobenzene[59] was isolated in quantitative yield. *2,5-Di-n-butoxymethyl-1,4-dimethoxybenzene*. 4-Butoxymethyl-2,5-di-methoxynitrobenzene (98 %): mp 61-62 °C; IR (KBr) υ_{max} 2960, 2943, 2868, 2851, 1514 (vs), 1399, 1353, 1278, 1215, 1157, 1111, 1030, 880, 800, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.2, 3), 1.35 (m, 2), 1.54 (m, 2), 3.51 (t, J = 6.3. 2), 3.76 (s, 3), 3.87 (s, 3), 4.49 (s, 2), 7.17 (s, 1), 7.32 (s, 1); ^{13}C NMR ($CDCl_3$) δ 13.70, 19.20, 31.48, 55.78, 66.61, 70.98, 106.92, 113.16, 135.11, 137.30, 147.72, 149.33; m/z 269 (M^+). The spectral data of the moiety cleaved from the arene was obtained by recording the nmr of the reaction crude and subtracting the signals due to the nitroarene (from the nmr spectra recorded after crystallization): ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 7.2, 3), 1.35 (m, 2), 1.54 (m, 2), 3.64 (t, J = 6.6, 2), 5.43 (s, 2); ^{13}C NMR ($CDCl_3$) δ 13.45, 19.14, 70.74, 95.16. On GC-MS analysis the highest mass corresponds to C_4H_9O. *2-Methoxymethyl-3,4,5-trimethyl-1,4-dimethoxybenzene* (V): The reaction yielded a mixture of 2-methoxymethyl-3,4,5-trimethyl-benzoquinone (53 %); mp 41-43 °C; IR (KBr) υ_{max} 2993, 2927, 2899, 2815, 1647, 1623, 1477, 1432, 1373, 1299, 1268, 1241, 1191, 1135, 1106, 1034, 944, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (s, 6), 2.03 (s, 3), 3.29 (s, 3), 4.26 (s, 2); ^{13}C NMR ($CDCl_3$) δ 12.14, 12.19, 12.22, 58.64, 64.56, 138.05, 140.37, 140.58, 144.14, 186.26, 187.60; m/z 194 (M^+); 2,4,5-trimethyl-3,6-dimethoxynitrobenzene (6 %) [note that nitroarene obtained in this experiment was the same as that obtained from the reaction of trimethyl-1,4-dimethoxybenzene with NO_2 in acetonitrile]; (2-methoxymethyl-dimethyl-1,4-dimethoxyphenyl)nitro methane (17 %); mp 78-81 °C; IR (KBr) υ_{max} 2982, 2943, 2924, 2900, 2883, 2869, 2828, 2801, 1553 (vs), 1463, 1371, 1256, 1191, 1117, 1092, 1074, 1000, 980, 949, 796, 643 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (s, 3), 2.22 (s, 3), 3.33 (s, 3), 3.67 (s, 3), 3.69 (s, 3), 4.51 (s, 2), 5.66 (s, 2); ^{13}C NMR ($CDCl_3$) δ 13.08, 13.27, 58.26, 61.17, 61.93, 66.24, 71.03,121.46, 128.86, 131.74, 134.10, 153.45, 154.52; m/z 269 (M^+), 193 (100) and unreacted starting material (23 %). *2,5-Di-tert-butyl-1,4-dimethoxybenzene*: 2,5-Dimethoxy-4-*tert*-butylnitrobenzene : IR (neat) υ_{max} 2986, 2966, 2955, 1680, 1532 (vs), 1444, 1360, 1312, 1290, 1218, 1189, 1055, 1014, 901, 790, 730 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.27 (s, 9), 3.88 (s, 3), 3.95 (s, 3), 7.07 (s, 1), 7.44 (s, 1); ^{13}C NMR ($CDCl_3$) δ 28.78, 34.32, 55.46, 56.77, 108.00, 113.37, 125.49, 147.01, 151.51, 153.90; *m/z* 239 (M^+). *2,6-Di-t-butyl-1,4-dimethoxybenzene*. 2,4-Di-t-butyl-3,6-dimethoxynitrobenzene: IR (neat) υ_{max} 3001, 2968, 2876, 1687, 1585, 1540 (vs), 1455, 1388, 1297, 1240, 1200, 1070, 1019, 911, 798, 752, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s, 9), 1.42 (s, 9), 3.60 (s, 3), 3.75 (s, 3), 6.89 (s, 1); ^{13}C NMR ($CDCl_3$) δ 31.29, 31.33, 36.17, 37.07, 56.41, 64.54, 110.41, 131.35, 135.14, 145.97, 146.17, 153.74; *m/z* 295 (M^+).

Solvent and Salt Effects on the Intramolecular Competition in Nitration/Dealkylation with Nitrogen Dioxide.

Reaction of 2,3,5-trimethyl-1,4-dimethoxybenzene (**If**) *with NO_2 in the presence of $PPN^+ NO_3^-$.* A cold (-78 °C) solution of **If** (0.2 mmol) and $PPN^+ NO_3^-$ (0.1 mmol) in dichloromethane (1 mL) was mixed with a cold solution of NO_2 (0.35 mmol, 0.2 M) and stirred at -78 °C for 20 min. The solvent and nitrogen oxides were removed *in vacuo* whilst warming to 25 °C. The crude residue, analyzed by GC and GC-MS, comprised unreacted **If** (88 %), 2,3,5-trimethyl-1,4-benzoquinone (6 %) and traces of sidechain nitration products.

Reaction of 2,3,5-trimethyl-1,4-dimethoxybenzene (**If**) *with NO_2 in the presence of n-$Bu_4N^+ PF_6^-$.* A cold (-78 °C) solution of **If** (0.2 mmol) and $Bu_4N^+ PF_6^-$ (0.2 mmol) in dichloromethane (1 mL) was mixed with a cold solution of NO_2 (0.35 mmol, 0.2 M) and stirred at -78 °C for 20 min. The solvent and nitrogen oxides were removed *in vacuo* whilst warming to 25 °C. The crude residue, analysed by GC-MS, contained 2,3,5-trimethyl-1,4-benzoquinone (80 %), 2,4,5-trimethyl-3,6-dimethoxynitrobenzene (8 %) and traces of sidechain nitration products. [Note that no starting material **If** was detected by GC-MS analysis.]

Reaction of 2,3,5-trimethyl-1,4-dimethoxybenzene (If) with NO_2 in acetonitrile. A cold acetonitrile solution of **If** (0.2 mmol, 0.2 M) was mixed with a solution of NO_2 (0.35 mmol, 0.2 M) in acetonitrile at -35 °C. The resultant yellow solution was stirred at this temperature for 10 min. The solvent was removed *in vacuo* and GC and GC-MS analysis of the crude residue indicated a mixture of 2,3,5-trimethylbenzoquinone (28 %), 2,4,5-trimethyl-3,6-dimethoxynitrobenzene (27 %), (trimethyl-1,4-dimethoxyphenyl)nitromethane (24 %) [tentatively identified by GC-MS: m/z (relative intensity) 225 (M^+, 8), 180 (12), 179 (100), 149 (18), 134 (29), 121 (29), 119 (41), 91 (33)] and trimethyl-1,4-dimethoxybenzylnitrate (7 %) [GC-MS: m/z (relative intensity) 241 (M^+, 21), 194 (67), 180 (100), 179 (67), 91 (63)].

Reaction of 2,3,5-trimethyl-1,4-dimethoxy-6-methoxymethylbenzene (V) with NO_2 in acetonitrile. A cold acetonitrile solution of **V** (0.2 mmol, 0.2 M) was mixed with a solution of NO_2 (0.35 mmol, 0.2 M) in acetonitrile at -35 °C. The resultant yellow solution was stirred at this temperature for 10 min. The solvent was removed *in vacuo* to yield: 2,3,5-trimethyl-6-methoxymethylbenzoquinone (5 %), 2,4,5-trimethyl-3,6-dimethoxynitrobenzene (46 %), and (dimethyl-2-methoxymethyl-1,4-dimethoxyphenyl)nitromethane (45 %).

Reaction of 5,8-dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene (IV) in n-hexane. A cold hexane solution of **IV** (0.2 mmol, 0.2 M) was mixed with a solution of NO_2 (0.35 mmol, 0.2 M) in hexane at -40 °C. The solution was stirred at this temperature for 10 min. and the solvent was removed *in vacuo*. The residue was analysed by GC and GC-MS and found to contain 16 % of unreacted **IV**, 1,4-methano-1,2,3,4-tetrahydronapthoquinone (84 %) and 5,8-dimethoxy-7-methyl-1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene (16 %).

Reaction of 5,8-dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene (IV) in acetonitrile. A cold acetonitrile solution of **IV** (0.2 mmol, 0.2 M) was mixed with a solution of NO_2 (4.0 mmol, 1.0 M) in acetonitrile at -40 °C. The mixture was stirred at this temperature for 20 min. In a slightly modified workup procedure,[60] a solution of 1,4-dimethoxybenzene (4.0 mmol, 0.2 M) in acetonitrile was added to the reaction mixture. [Dimethoxybenzene reacts with excess nitrogen dioxide to give nitrodimethoxybenzene.] The reaction mixture was warmed to room temperature while stirring. After evaporation of the solvent *in vacuo*, the residue was analyzed by GC, GC-MS and ^1H NMR spectroscopy. The major product was 5,8-dimethoxy-7-methyl-

1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene (80 %) (previously formed in minor amounts) together with 6-methyl-1,4-methano-1,2,3,4-tetrahydronapthoquinone (20 %).

Reaction of 5,8-dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene (IV) in the presence of $Bu_4^+ PF_6^-$ in acetonitrile. In an otherwise identical reaction $Bu_4^+ PF_6^-$ (20 equiv.) was added to the solution of the IV before it was mixed with the solution of NO_2. After workup [with addition of dimethoxybenzene (4 mmol) as described above] GC-MS and NMR analysis of the crude residue afforded: 6-methyl-1,4-methano-1,2,3,4-tetrahydronapthoquinone (13 %) and 5,8-dimethoxy-7-methyl-1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene (87 %).

Reaction of 5,8-dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronapthalene (IV) in the presence of $PPN^+ NO_3^-$ in acetonitrile. A third reaction in acetonitrile was performed with $PPN^+ NO_3^-$ (8 equiv.) added to the cold solution of IV before it was mixed with the solution of NO_2. After workup [with addition of dimethoxybenzene (4 mmol) as described above] GC-MS and NMR analysis of the crude residue indicated: 6-methyl-1,4-methano-1,2,3,4-tetrahydronapthoquinone (72 %) and 5,8-dimethoxy-7-methyl-1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene (28 %).

Intermolecular Competition between Nitration and Dealkylation of Dialkoxybenzenes with Nitrogen Dioxide

Reaction of 4-octyloxyanisole (IId) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene with NO_2 in dichloromethane. A cold (-78 °C) dichloromethane solution of nitrogen dioxide (1.0 mL, 0.2 M) was added to a well-stirred cold (-78 °C) solution of the dialkoxybenzenes (0.2 mmol each) in dichloromethane (10 mL). The pale yellow solution was stirred at -78 °C for 1 min., warmed to room temperature and stirred for a further 15 min. The solvent was evaporated and the residue, analyzed by ^1H NMR and GC-MS, contained: 4-octyloxynitroanisole (3:1 mixture of isomers) (0.05 mmol), 1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthraquinone (0.11 mmol), **IId** (0.15 mmol) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene (0.09 mmol).

Reaction of 4-octyloxyanisole (IId) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene with NO_2 in acetonitrile. A cold (-35 °C) solution of nitrogen dioxide (1.0 mL, 0.2 M) in acetonitrile was added to a cold (-35 °C) solution of the dialkoxybenzenes (0.2 mmol each) in acetonitrile (10 mL). The pale yellow solution was stirred at -40 °C for 1 min, warmed to room temperature, and stirred for a further 15 min. The solvent was removed *in vacuo*, and the crude residue, analyzed by GC and ^1H NMR, contained: 4-octyloxynitroanisole (3:1 mixture of isomers) (0.13 mmol), 1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthraquinone (<0.01 mmol), **IId** (0.07 mmol) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene (0.20 mmol).

Reaction of 1,4-dimethoxybenzene (Ia) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene with NO_2 in dichloromethane. The dialkoxybenzenes (0.2 mmol each) were reacted with NO_2 (0.2 mmol, 0.1M) in dichloromethane solution as described above. The crude residue contained: **Ia** (0.20), 1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthraquinone (0.10 mmol), 2,5-dimethoxynitrobenzene (<0.01 mmol) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene (0.10 mmol).

Reaction of 1,4-dimethoxybenzene (Ia) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene with NO_2 in acetonitrile. The dialkoxybenzenes (0.2 mmol each) were reacted with NO_2 (0.2 mmol,

0.1M) in acetonitrile solution as described above. The products were: **Ia** (0.07), 1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthraquinone (<0.01 mmol), 2,5-dimethoxynitrobenzene (0.13 mmol) and 9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene (0.20 mmol).

Reaction of 1,4-Dimethoxybenzene with Nitrogen Dioxide in the Presence of Dioxygen

Measurement of oxygen uptake. 1,4-Dimethoxybenzene (0.931 mg, 6.74 mmol) was added under a flow of oxygen to a dichloromethane solution of NO_2 (5.40 mmol, 20 mL) cooled to -23 °C in a carbon tetrachloride / dry-ice bath. The flask was immediately connected to a pressure equalized gas burette filled with oxygen. The temperature was rigorously maintained at -23 °C and the uptake of oxygen monitored [t = 3 min, 4.0 mL; t = 5 min, 7.7 mL; t = 15 min, 22.5 mL; t = 25 min, 26.6 mL; t = 35 min, 29.3 mL; t = 47 min, 29.8 mL]. After 50 min there was no further consumption of oxygen (total O_2 = 1.33 mmol). The bright yellow solution was evaporated and dried *in vacuo*. The yellow residue (1.17 g) was shown by ^1H NMR and GC-MS to comprise 2,5-dimethoxynitrobenzene (5.37 mmol) and 1,4-dimethoxybenzene (1.37 mmol). The water (2.7 mmol) was not quantified.

Formation and Reactions of 1,4-Dimethoxybenzene Radical Cation ($Ia^{+\cdot}$) with Nitrogen Oxides

Formation of 1,4-dimethoxybenzene radical cation with NO^+ BF_4^-. A quartz cuvette fitted with a side arm and a Schlenk adaptor was charged with NO^+ BF_4^- (5 mg, 0.04 mmol) and a solution of 1,4-dimethoxybenzene (5 mg, 0.01 mmol) in dichloromethane was added under an argon atmosphere. The colorless suspension was stirred for 30 min. to yield a yellow-green solution of $Ia^{+\cdot}$ (λ_{max} = 433, 460 nm, see Figure 2). UV-vis spectral analysis of the head gas revealed the characteristic absorbances of NO at λ_{max} = 204, 214 and 226 nm.

Spectral measurement of the temperature dependence of the reaction of $Ia^{+\cdot}$ with NO. When the solution of $Ia^{+\cdot}$, prepared as above, was cooled to -78 °C the intensity of the yellow color decreased. There was a concommitant increase in the absorbance at λ_{max} = 366 nm which was due to the [**Ia**, NO^+] charge-transfer complex.[30] The UV-vis absorption spectum was recorded at several intermediate temperatures and showed an isosbestic point at λ = 410 nm (see Figure 2).

In a separate experiment, the same phenomenon was observed with 5,8-dimethoxy-1,4-methano-1,2,3,4-tetrahydronapthalene radical cation. Thus, the arene (5.2 mg, 0.02 mmol) was added to a suspension of NO^+ BF_4^- (5 mg, 0.04 mmol) in dichloromethane (6 mL) in a quartz cuvette fitted with a Schlenk adaptor. The solution was stirred for 30 min. and a yellow-green solution of 5,8-dimethoxy-1,4-methano-1,2,3,4-tetrahydro-napthalene radical cation was obtained (λ_{max} = 450, 476 nm). [Note that the same radical cation was prepared from $AlCl_3$[61] and $SbCl_5$[62].] On successive cooling of the solution, the absorbance of the radical cation at λ_{max} = 450, 476 nm decreased with a concommitant increase in the absorbance at λ = 350 nm due to the [ArH, NO^+] charge-transfer complex. The isosbestic point at λ = 422 nm confirmed the temperature dependent electron transfer. This remarkable temperature effect was clearly dependent on the presence of nitric oxide. In a separate experiment, argon was continually bubbled through the stirred mixture of arene and NO^+. In this way the NO formed on oxidation of the arene was entrained. The resultant yellow-green solution of the radical cation was unchanged (UV-vis) on cooling to -78 °C .

Reaction of Ia with $NO^+BF_4^-$ in the presence of dioxygen. A 1-cm quartz cuvette equipped with a sidearm and Teflon needle valve was charged with a solution of 1,4-dimethoxybenzene (276 mg, 2.0 mmol) in dichloromethane (10 mL). The solution was cooled to -78 °C in a dry-ice / acetone bath and NO^+ BF_4^- (117 mg, 1.0 mmol) was added. The suspension was warmed to 25 °C and stirred for 30 min. The dark yellow-green solution thus obtained was cooled to -15 °C in an ice / acetone bath. The solution was exposed to an oxygen-filled balloon and the characteristic brown color of nitrogen dioxide was apparent above the solution. After stirring for 15 min., the dark brown mixture was treated with aqueous bicarbonate (25 mL). The clear yellow organic layer was separated and dried. The solvent was removed *in vacuo*. The residue, analyzed by ^1H NMR and GC-MS, comprised: 2,5-dimethoxynitrobenzene (176 mg, 0.97 mmol) and 1,4-dimethoxybenzene (136 mg, 0.99 mmol).

Reaction of $Ia^{+\cdot}$ with nitrogen dioxide. A suspension of NO^+ $SbCl_6^-$ (731 mg, 2.0 mmol) in dichloromethane (20 mL) in a 1-cm quartz cuvette equipped with a sidearm and Teflon needle valve was cooled to -78 °C. Dimethoxybenzene (276 mg, 2.0 mmol) was added to the suspension under a flow of argon. The pale yellow mixture was brought to 25 °C and stirred to yield a dark yellow-green solution. The nitric oxide produced (spectrally observed by UV-vis) was entrained by bubbling argon through the solution. The resultant yellow solution was cooled in a dry-ice / acetone bath. A prechilled solution of nitrogen dioxide (10 mL, 0.2 M) was added dropwise to the stirred solution of $Ia^{+\cdot}$ and the reaction mixture warmed to 25 °C over 15 min. The reaction was worked up as above to afford a yellow residue which was essentially pure (^1H NMR and GC-MS) 2,5-dimethoxynitrobenzene (352 mg, 1.92 mmol).

Reaction of 5,8-dimethoxy-1,4-methano-1,2,3,4-tetrahydronapthalene radical cation with nitrate. A suspension of nitrosonium tetrafluoroborate (119 mg, 1.0 mmol) in dichloromethane (20 mL) in a 1-cm quartz cuvette equipped with a sidearm and Teflon needle valve was cooled to -78 °C. 5,8-Dimethoxy-1,4-methano-1,2,3,4-tetrahydronapthalene (412 mg, 2.0 mmol) was added to the suspension under a flow of argon. The suspension was brought to 25 °C while stirring to yield a dark yellow-green solution. The nitric oxide produced was entrained by bubbling argon through the solution. The resultant solution was cooled to -78 °C in a dry-ice / acetone bath. A prechilled solution of PPN^+ NO_3^- (1.20 g, 2 mmol) was added to the stirred solution of the radical cation. The color immediately bleached to yield a pale yellow solution. After stirring for 15 min. the solvent was removed *in vacuo*. The residue was extracted with ether (2 x 20 mL) and the ether extracts were passed through a short pad of silica gel to remove the PPN salt. The solvent was removed *in vacuo*. The residue which was analyzed by quantitative ^1H NMR and GC-MS contained unreacted 5,8-dimethoxy-1,4-methano-1,2,3,4-tetrahydronapthalene (1.30 mmol); 5,8-dimethoxy-1,4-methano-1,2,3,4-tetrahydro-6-nitronaphthalene (0.06 mmol) and 5,5',8,8'-tetramethoxy-1,1',4,4'-*bis*-methano-1,2,3,4,1',2',-3',4'-octahydro-2,2'-binapthyl (0.62 mmol) [26] 1,1',4,4'-*bis*-Methano-5,5',8,8'-tetramethoxy-1,2,3,4,-1',2',3',4'-octahydro-2,2'-binapthyl: ^1H NMR ($CDCl_3$) δ 1.18 (m, 4), 1.46 (m, 2), 1.70 (m, 2), 1.89 (m, 4), 3.60 (m, 4), 3.79 (s, 12), 6.59 (s, 2); ^{13}C NMR ($CDCl_3$) δ 26.46, 26.97, 39.80, 41.06, 55.71, 60.89, 111.77, 129.89, 135.60, 140.57, 145.57, 148.40; *m/z* 406 (M^+).

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60. The excess nitrogen dioxide in acetonitrile reacted further with the initial product, 5,8-dimethoxy-7-methyl-1,4-methano-1,2,3,4-tetrahydro-6-nitronapthalene, to afford a complex mixture of products. The workup procedure was thus altered by adding 1,4-dimethoxybenzene at the end of the reaction time to consume the excess nitrogen dioxide.
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