



Substituent effects in the oxidation of 2-alkyl-1,4-dialkoxybenzenes with ceric ammonium nitrate



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ARTICLE INFO

Article history:

Received 7 October 2016

Revised 2 November 2016

Accepted 8 November 2016

Available online 9 November 2016

Keywords:

Quinone

Diquinone

Ceric ammonium nitrate

Oxidation

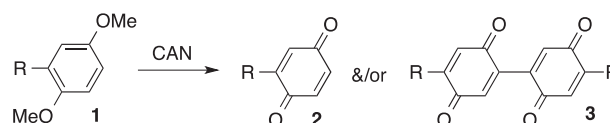
ABSTRACT

Increased steric size of alkyl groups and the presence of coordinating atoms on alkoxy groups have both been found to contribute to decreasing yields of diquinones upon reaction of 2-alkyl-1,4-dialkoxybenzenes with CAN. The overall hydrophilicity of the substrates does not appear to be a significant factor in determining the diquinone yield for these reactions.

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Treatment of 1,4-dimethoxybenzene derivatives **1** with ceric ammonium nitrate (CAN) is known to result in their oxidation to the corresponding quinones **2**.^{1,2} Diquinones **3** are occasionally observed as byproducts of such reactions, and in some instances can even be the major product.^{1–3} We have been interested in determining some of the factors that govern quinone/diquinone product ratios for such reactions (Scheme 1).⁴

Previously we have noted that reaction conditions (solvents, order of addition, etc.) can affect the isolated yields of diquinones in these oxidations.^{5,6} For example, it was found that addition of acetonitrile solutions of the aromatic substrate to aqueous solutions of CAN gave higher yields of diquinone **3** than did additions of aqueous solutions of CAN to acetonitrile solutions of the aromatic substrate. Based on the presumed mechanisms of these reactions (summarized in Scheme 2) one could imagine the fate of radical cationic intermediate **4** playing a key role in determining the quinone/diquinone product ratio of the reaction (though other factors such as extent of reversibility of the various steps and relative intermediate stability could also be significant). Attack of intermediate **4** by aryl ether **1** could lead to intermediate **5**, which could eventually form diquinone **3** after a series of additional steps. On the other hand, if intermediate **4** undergoes hydrolysis, quinone **2** would be the eventual product. (It has been shown that **2** does not oxidize to **3** under such reaction conditions.⁵ Thus quinone/diquinone product ratios would seem to be dependent upon the



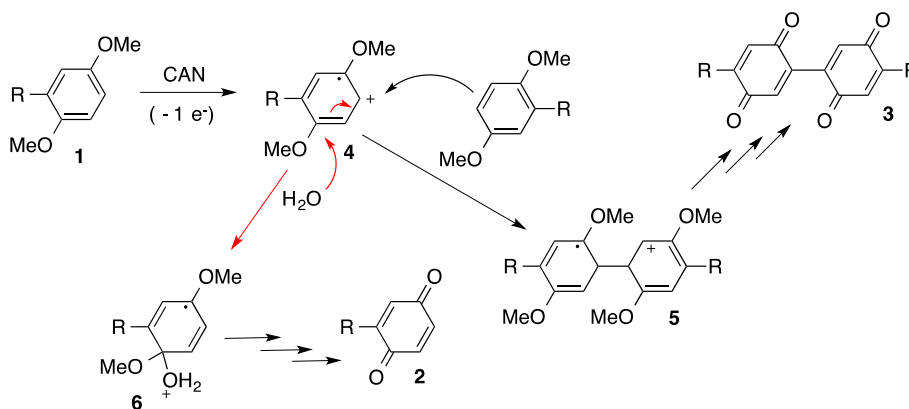
Scheme 1. Oxidation of 1,4-dimethoxybenzene derivatives with CAN.

relative ease with which the two nucleophiles (aryl ether and water) react with common intermediate **4**.

One possible explanation for increased diquinone formation upon addition of the aryl ether to the CAN is that as the aryl ether solution is added dropwise to the aqueous CAN, aggregates of the aryl ether molecules could form, due to their low solubility in water. This might be expected to increase the likelihood that intermediate **4** would react with aryl ether **1** instead of water, and therefore favor diquinone formation (compared to the situation in which aqueous CAN is added slowly to an acetonitrile solution of the aryl ether, during which no such aggregation would be expected to occur). If this were true, it would suggest that quinone/diquinone product ratios might be affected by the aqueous solubility of the aryl ether substrate, with more hydrophilic substrates favoring quinone formation and more hydrophobic substrates favoring diquinone formation. We therefore prepared a series of substrates in order to test this hypothesis. Since earlier work had indicated that the electron density of the aromatic ring could also influence quinone/diquinone product ratios,⁵ we limited our substrates to 2-alkyl-1,4-dialkoxybenzenes in order to minimize such electronic effects.

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Scheme 2. Partial mechanisms for the formation of quinones and diquinones.

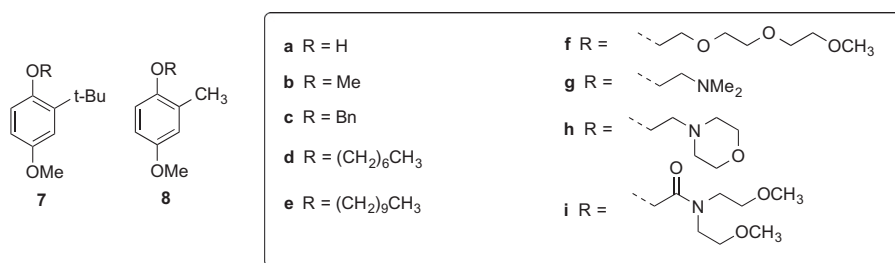


Fig. 1. Initial 1,4-dialkoxybenzene derivatives investigated.

Due to the ready availability of BHA **7a**⁷ and the fact that 2-*t*-butyl-1,4-dimethoxybenzene **7b** produced significant quantities of both quinone and diquinone upon treatment with CAN, we initially investigated the series of substrates **7** shown in Fig. 1. We also investigated the analogous series of compounds **8**, since **8b** had previously been shown by us^{5,6} and others^{1,2} to give almost exclusively the diquinone product upon treatment with CAN under typical reaction conditions.

If substrate hydrophilicity were to have a significant effect on quinone/diquinone product ratios, one would expect **7c–7e** to have increased diquinone formation compared to **7b**, while **7f–7i** would be expected to have decreased diquinone formation. As can be seen from the data in Table 1, however, this was not observed, leading us to conclude that substrate hydrophilicity is not a major factor in determining quinone/diquinone product ratios.⁸

There were several striking observations upon examining the data in Table 1, however. One is the complete absence of diquinone formation when substrate **7i** was treated with CAN. Instead, the corresponding quinone **2** was obtained in 79% yield. (We will discuss this observation in more detail shortly). Secondly, with a few exceptions, the substrates with a methyl group as the alkyl group (**8**) generally gave higher diquinone yields than their *t*-butyl counterparts **7**. This prompted a brief investigation into the effects of the steric size of the alkyl group on diquinone yields. 1,4-

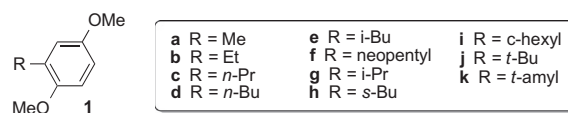


Fig. 2. Additional 1,4-dimethoxybenzene derivatives investigated.

Dimethoxybenzene derivatives **1** (Fig. 2) were prepared and were allowed to react with CAN under similar reaction conditions⁹ as used for substrates **7** and **8**. Results of these oxidations are presented in Table 2.

Based on the data presented in Table 2, the steric size of the alkyl group at C-2 does appear to have some effect on diquinone yield. While the methyl-substituted compound **1a** produced the corresponding diquinone **3** in approximately 90% yield, each additional substitution at the benzylic carbon of the substrate lowered the diquinone yield by approximately 15%. Substrates bearing primary alkyl groups (**1b–1f**) gave yields in the range of 75%, while those with secondary alkyl groups (**1g–1i**) produced diquinones in the 60% range, and those bearing a tertiary alkyl group (**1j** & **1k**) had diquinone yields of around 45%. If one looks at the five substituents that are nominally based on propyl groups (**c**, **e**, **f**, **h**, & **k**), one sees that while substitution at the α carbon results in

Table 1
Diquinone Percent Yields^a Upon Treatment of **7** and **8** with CAN.

Substituent:	b	c	d	e	f	g	h	i
Substrate 7 :	46	43	49	49 ^b	46	61	37	0
Substrate 8 :	92	57	nd	41 ^b	25	74	66	25

nd = not determined.

^a Isolated yields.

^b Substrate not completely soluble in volume of acetonitrile used, therefore added as a suspension.

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