Effects of Reaction Conditions on Quinone/Diquinone Product Ratios in the Oxidation of 1,4-Dimethoxybenzene Derivatives with Ceric Ammonium Nitrate

Brian E. Love, Brian C. Duffy, Alexander L. Simmons

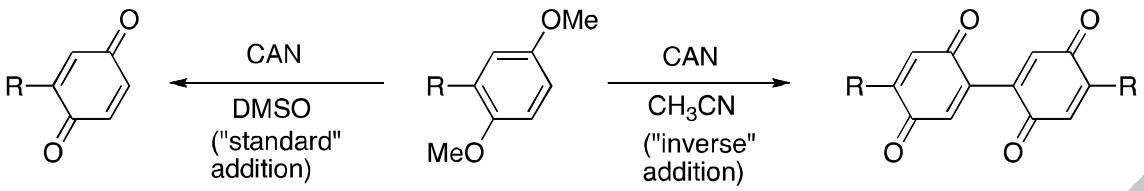
PII: S0040-4039(14)00238-X
DOI: http://dx.doi.org/10.1016/j.tetlet.2014.02.017
Reference: TETL 44204

To appear in: *Tetrahedron Letters*

Received Date: 26 November 2013

Please cite this article as: Love, B.E., Duffy, B.C., Simmons, A.L., Effects of Reaction Conditions on Quinone/Diquinone Product Ratios in the Oxidation of 1,4-Dimethoxybenzene Derivatives with Ceric Ammonium Nitrate, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/10.1016/j.tetlet.2014.02.017

Graphical Abstract



Reaction conditions can be used to favor either quinone or diquinone formation upon treatment of 2-alkyl-1,4-dimethoxybenzenes with ceric ammonium nitrate.

Effects of Reaction Conditions on Quinone/Diquinone Product Ratios in the Oxidation of 1,4-Dimethoxybenzene Derivatives with Ceric Ammonium Nitrate

Brian E. Love,* Brian C. Duffy and Alexander L. Simmons

Department of Chemistry, East Carolina University, Greenville, NC, 27858, USA

_____

* Corresponding author. Tel: +1 252 328 9778; fax: +1 252 328 6210

E-mail address: loveb@ecu.edu

Abstract

Proper choice of reaction conditions allows formation of either the quinone or corresponding diquinone as the major product upon treatment of 2-alkyl-1,4-dimethoxybenzenes with ceric ammonium nitrate.

Keywords

Quinone, Diquinone, Ceric Ammonium Nitrate, Oxidation

Quinones represent a chemically interesting and biologically significant class of compounds.[1] Though benzoquinones can be prepared by a variety of means,[1,2] they are perhaps most commonly synthesized through treatment of hydroquinone ethers with ceric ammonium nitrate (CAN).[3] This same reaction, however, is likewise one of the most common means of preparing diquinones[3] (though other methods are also known).[4] Treatment of hydroquinone ethers with CAN thus can often lead to mixtures of quinones and diquinones as products.

We are seeking to determine some of the parameters that influence quinone/diquinone ratios in the product mixtures of such reactions. Preliminary results[5,6] suggest that the nature of the alkoxy groups, other substituents present on the benzene ring, and reaction conditions such as solvent, concentration, and order of addition can all affect this ratio. One aim of this project is the development of reaction protocols that would allow one to selectively produce either the quinone or the corresponding diquinone from the same 1,4-dimethoxybenzene precursor with minimal contamination by the other possible product. Herein we report our findings toward that end.

We chose 2-*tert*-butyl-1,4-dimethoxybenzene and 2,5-dimethoxytoluene as our initial two test substrates. The former was chosen due to its ease of preparation from inexpensive starting materials[7] and the fact that under "traditional" conditions[3a] comparable amounts of quinone and diquinone were produced, yet were readily isolated in fairly pure form. The 2,5-dimethoxytoluene was utilized owing to its commercial availability. A variety of reaction conditions were investigated (see Tables 1 and 2) though in all reactions 2.0 mmol of substrate were allowed to react with 7.0 mmol of CAN. Solvents were dispensed using graduated pipets to ensure greater control over precise solvent volumes. With respect to the order of addition, we have chosen to use the term "standard" to refer to addition of the CAN to the substrate, and "inverse" to describe addition of the substrate to the CAN.

Table 1 shows the results obtained using 2-*tert*-butyl-1,4-dimethoxybenzene as a substrate, arranged according to the mole ratios of the products obtained.[8] One trend that emerges is that quinone formation is generally favored by the "standard" mode of addition, whereas "inverse" addition tends to

give higher percentages of diquinone formation. This is consistent with earlier results,[5] and is supported by direct comparison of reactions that varied only in their mode of addition. Compare, for example, entries 3 & 8, 4 & 10, 7 & 22, 14 & 20, 15 & 24, and 18 & 23--in all cases the reaction utilizing "standard" addition provided a higher proportion of quinone in the product mixture than did the corresponding reaction using "inverse" addition. It would appear that the nature of the solvent also has some effect on product ratios, but we have not conducted a sufficient number of experiments to clearly identify this effect or determine a definitive trend.

When CAN was added directly as a solid to the arene solution (entries 1 and 2), no diquinone formation was observed, though the product mixtures contained incompletely oxidized compounds that still possessed methoxy groups (as evidenced by their ^{1}H NMR spectra). These side products included, but were not limited to, 5-nitro-2-*tert*-butyl-1,4-dimethoxybenzene, and were also present in the product mixtures of many of the reactions in which DMSO was used as solvent (Entries 3, 5, 7, 8 and 22). Initially we thought that DMSO (or perhaps impurities in it, such as dimethylsulfide) was being oxidized by the CAN, thus reducing the amount of oxidant available to react with the arene substrate. Use of larger excesses of CAN failed to remove these impurities from the product mixtures, however. Such by-products were also observed when 1,2-dimethoxyethane (DME) was used as solvent (entry 2).

Table 1. Oxidation of 2-*tert*-butyl-1,4-dimethoxybenzene by CAN

Entry	Substrate Solvent	CAN Solvent	Mode of Addition	Quinone: Diquinone Mole Ratio	Protocol Designation
1	10.0 mL DMSO	none	Standard	quinone only	**A**
2	10.0 mL DME	none	Standard	quinone only	
3	10.0 mL DMSO	5.0 mL H2O	Standard	48 : 1	**B**
4	14.0 mL THF	7.0 mL H2O	Standard	27 : 1	**C**
5	14.0 mL THF + 1.0 mL DMSO	7.0 mL H2O	Standard	23 : 1	
6	14.0 mL EtOAc	7.0 mL H2O	Standard	10 : 1	
7	2.0 mL DMSO	7.0 mL H2O	Standard	6 : 1	
8	10.0 mL DMSO	5.0 mL H2O	Inverse	6 : 1	
9	7.0 mL THF	7.0 mL H2O + 7.0 mL THF	Inverse	5 : 1	
10	14.0 mL THF	7.0 mL H2O	Inverse	5 : 1	
11	21.0 mL acetone + 7.0 mL H2O	14.0 mL H2O	Standard	4 : 1	
12	14.0 mL CH3CN	7.0 mL H2O	Standard	2.8 : 1	
13	3.5 mL THF	3.5 mL H2O	Inverse	2.7 : 1	
14	1.0 mL THF	3.5 mL H2O	Standard	2.5 : 1	
15	7.0 mL CH3CN	7.0 mL H2O	Standard	2.3 : 1	**Traditional**
16	3.5 mL CH3CN	7.0 mL H2O	Inverse	1.7 : 1	
17	2.0 mL THF	7.0 mL H2O	Inverse	1.7 : 1	
18	2.0 mL CH3CN	3.5 mL H2O	Standard	1.6 : 1	
19	4.0 mL CH3CN	7.0 mL H2O	Inverse	1.5 : 1	
20	1.0 mL THF	3.5 mL H2O	Inverse	1.2 : 1	**D**
21	3.5 mL CH3CN	3.5 mL H2O	Inverse	1 : 1	
22	2.0 mL DMSO	7.0 mL H2O	Inverse	1 : 1	
23	2.0 mL CH3CN	3.5 mL H2O	Inverse	1 : 1.3	**E**
24	7.0 mL CH3CN	7.0 mL H2O	Inverse	1 : 1.9	**F**

Results obtained using 2,5-dimethoxytoluene as the substrate (Table 2) were somewhat similar, though this compound displayed a much greater tendency toward diquinone formation, as had been observed earlier by others.[3] This increased diquinone formation is clearly seen through comparison of reactions run under identical conditions on the two test substrates. As was noted with 2-*tert*-butyl-1,4-dimethoxybenzene, quinone formation tended to be favored by the "standard" mode of addition. Compare, for example, entries 3 & 4, 5 & 8, 7 & 12, 10 & 14, and 11 & 15--in each of these comparisons the reaction utilizing "standard" addition once again provided a higher proportion of quinone in the

product mixture than did the corresponding reaction using "inverse" addition. In only one pair of reactions was this not the case (entries 13 & 16).[9]

Incompletely oxidized products were once again observed in many of the reactions that tended to favor quinone formation (entries 2 through 6), though were not observed in every reaction involving DMSO. Products of reactions listed in entries 1, 7 and 12, for example, contained very little if any such impurities.

Table 2. Oxidation of 2,5-dimethoxytoluene by CAN

Entry	Substrate Solvent	CAN Solvent	Mode of Addition	Quinone: Diquinone Mole Ratio	Protocol Designation
1	10.0 mL DMSO	none	Standard	20 : 1	**A**
2	10.0 mL DME	none	Standard	10 : 1	
3	10.0 mL DMSO	5.0 mL H2O	Standard	4 : 1	**B**
4	10.0 mL DMSO	5.0 mL H2O	Inverse	1.2 : 1	
5	14.0 mL THF	7.0 mL H2O	Standard	1 : 2.4	**C**
6	10.0 mL THF	14.0 mL H2O	Standard	1 : 4	
7	2.0 mL DMSO	7.0 mL H2O	Standard	1 : 6	
8	14.0 mL THF	7.0 mL H2O	Inverse	1 : 7	
9	14.0 mL EtOAc	7.0 mL H2O	Standard	1 : 9	
10	1.0 mL THF	3.5 mL H2O	Standard	1 : 12	
11	7.0 mL CH3CN	7.0 mL H2O	Standard	1 : 14	**Traditional**
12	2.0 mL DMSO	7.0 mL H2O	Inverse	1 : 14	
13	2.0 mL CH3CN	3.5 mL H2O	Inverse	1 : 18	**E**
14	1.0 mL THF	3.5 mL H2O	Inverse	1 : 20	**D**
15	7.0 mL CH3CN	7.0 mL H2O	Inverse	1 : 22	**F**
16	2.0 mL CH3CN	3.5 mL H2O	Standard	1 : 58	

Based on these preliminary results, some "favored protocols" emerged. Addition of CAN (both neat and as an aqueous solution) to DMSO solutions of the arene (entries 1 and 3 in both Tables 1 and 2) reliably gave high percentages of quinone as the product. Replacement of DMSO with THF (entry 4 in Table 1 and entry 5 in Table 2) also gave reasonable quantities of quinone product (moreso with 2-*tert*-butyl-1,4-dimethoxybenzene than 2,5-dimethoxytoluene) and offered the advantage of reduced

contamination by incompletely oxidized by-products. These "quinone favoring protocols" are designated A, B and C as indicated in the tables.[10]

Diquinone formation, on the other hand, appeared to be favored by "inverse" addition of the arene, dissolved in acetonitrile, to an aqueous solution of CAN (entries 23 and 24 in Table 1, and entries 13 and 15 in Table 2). Replacement of acetonitrile with a minimal amount of THF (entries 20 and 14 in Tables 1 and 2, respectively) also produced significant amounts of diquinone. These "diquinone favoring protocols" are designated D, E and F as indicated in the tables.

We next sought to test the generality of these protocols on a wider range of substrates. Since the electronic nature of substituents also appears to play a role in determining quinone/diquinone product ratios, we restricted our substrates to 2-alkyl-1,4-dimethoxybenzene derivatives in an attempt to reduce the influence of this variable. Each substrate was subjected to "traditional" reactions conditions (defined as addition of an aqueous CAN solution (1.0 M) to the arene dissolved in an equal volume of acetonitrile)[11] as well as one or more of our "favored protocols" for quinone and diquinone formation. In all reactions, the addition of one reagent to the other was allowed to occur over a period of 10-15 minutes. Once the addition was complete, the reaction mixture was allowed to stir for 1 hour, after which time it was diluted with water, and any precipitate that formed was collected by filtration--this was usually the diquinone, which was typically obtained in a high state of purity. Extraction of the filtrate with ether allowed isolation of the corresponding quinones, though they were often contaminated by impurities from which they were difficult to separate. In our hands, neither recrystallization nor column chromatography provided the quinones in analytically pure form. Quinone yields reported are thus approximate yields based on product weights coupled with purity estimates taken from NMR data. The results of these studies are summarized in Table 3.

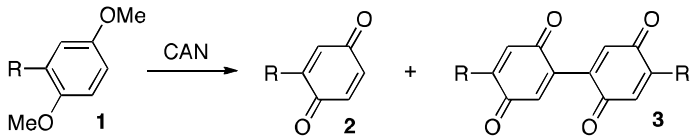


Table 3. Oxidation of 2-alkyl-1,4-dimethoxybenzene derivatives by CAN

	Quinone-Favoring Protocols			*Traditional Protocol*			*Diquinone-Favoring Protocols*		
R	**Protocol Used**	**Yield of 2 (%)**	**2 : 3 Mole Ratio**	**Yield of 2 (%)**	**2 : 3 Mole Ratio**	**Yield of 3 (%)**	**2 : 3 Mole Ratio**	**Yield of 3 (%)**	**Protocol Used**
Me	A	72	20 : 1	3	1 : 14	89	1 : 20	82	D
Me	B	42	4 : 1				1 : 18	90	E
Me	C	12	1 : 2.4				1 : 22	93	F
Et	B	63	17 : 1	8	1 : 4.7	73	diquinone only	84	E
Et	C	18	1 : 1				1 : 20	75	F
n-Pr	A	80	> 50 : 1	20	1 : 1.7	67	1 : 3.9	77	E
n-Pr	B	63	19 : 1						
n-Pr	C	20	1 : 1.2						
n-Bu	B	58	13 : 1	17	1 : 1.9	64	1 : 6.1	78	F
n-Bu	C	35	2.6 : 1						
i-Bu	B	68	30 : 1	17	1 : 1.9	67	1 : 3.1	76	F
i-Bu	C	36	2 : 1						
t-Bu	A	70	> 50 : 1	42	2.3 : 1	37	1.2 : 1	55	D
t-Bu	B	73	48 : 1				1 : 1.3	55	E
t-Bu	C	82	27 : 1				1 : 1.9	46	F
n-pentyl	A	70	> 50 : 1	14	1 : 2.4	65	1 : 12	80	E
n-pentyl	B	63	12 : 1						
n-pentyl	C	25	1 : 1						
n-heptyl	B	51	14 : 1	12	1 : 2.4	59	1 : 4.4	64	E
n-heptyl	C	33	2.3 : 1				1 : 19	93	F
n-nonyl	B	28	26 : 1	22	1: 1.3	57	1 : 3.8	73	E
n-nonyl	C	32	3.3 : 1				1 : 2.9	69	F
n-undecyl	C	39	2.3 : 1	21	1 : 1.8	75	1 : 63	96	D

In all cases, mole ratio enhancements were observed by using one of the "favored" protocols in place of the "traditional" protocol. In most reactions, use of "diquinone-favoring protocols" improved yields of the diquinone product by 10% or more over the "traditional" protocol. The exception is when

2,5-dimethoxytoluene was used as the substrate, owing to the high diquinone yield obtained using the traditional protocol. Even larger yield improvements were observed using "quinone-favoring protocols," again in part due to the low yields of such compounds obtained following the traditional protocol. Though yield improvements were often significant, total yields were low when substrates containing large lipophilic sidechains were employed. Additionally, for the most lipophilic substrate tested (the undecyl-substituted compound), reduced solubility in acetonitrile and DMSO restricted protocols to those utilizing THF as solvent if substrate molar concentrations were to be held constant. Owing to the pronounced biological activity of quinones possessing long nonpolar sidechains[12] we are continuing to work on the development of methodologies that would allow the preparation of such compounds in greater yield and higher states of purity. It is gratifying, however, that the current methods do allow easy preparation of the corresponding diquinones, which are of interest in their own right.[13]

In summary, quinone:diquinone product ratios from the CAN oxidation of 1,4-dimethoxybenzene derivatives can be shifted to favor either product by proper choice of reaction conditions. Diquinones were generally obtained in a high state of purity, though most of the quinones were contaminated with incompletely oxidized products from which they were difficult to separate.

Supplementary data

Supplementary data (experimental procedures and characterization data) associated with this article can be found in the online version at doi: xxx

References and notes

1) Patai, S.; Rappoport, Z. (editors), *The Chemistry of the Quinonoid Compounds*, Vol. 2, Pt. 1 & 2, Wiley, Chichester (1988).

2a) Akai, S.; Kita, Y. Recent Progress in the Synthesis of *p*-Quinones and *p*-Dihydroquinones Through Oxidation of Phenol Derivatives. A Review. *Organic Preparations and Procedures International*, **1998**, *30*, 603-629. b) Tomatsu, A.; Takemura, S.; Hashimoto, K. Nakata, M. Synthesis of Quinones from

Hydroquinone Dimethyl Ethers. Oxidative Demethylation with Cobalt(III) Fluoride. *Synlett* **1999**, 1474-1476.

3a) Jacob III, P.; Callery, P. S.; Shulgin, A. T.; Castagnoli, Jr., N. A Convenient Synthesis of Quinones from Hydroquinone Methyl Ethers. Oxidative Demethylation with Ceric Ammonium Nitrate. *Journal of Organic Chemistry* **1976**, *41*, 3627-3629; b) Ali, M. H.; Niedbalski, M.; Bohnert, G.; Bryant, D. Silica-Gel Supported Ceric Ammonium Nitrate (CAN): A Simple and Efficient Solid-Supported Reagent for Oxidation of Oxygenated Aromatic Compounds to Quinones. *Synthetic Communications* **2006**, *36*, 1751-1759.

4a) Paraskevas, S. M.; Konstantinidis, D.; Vassilara, G. Oxidation of hydroquinones with oxygen in the presence of bis(1,3-propanediaminato)copper(II) chloride. *Synthesis* **1988**, 897-899. b) Rao, D. V.; Ulrich, H.; Sayigh, A. A. R. Synthesis of benzoquinone-1,4-aldehyde diacetate. *Journal of Organic Chemistry* **1975**, *40*, 2548-2549. c) Posternak, T.; Alcalay, W.; Luzzati, R.; Tardent, A. Biphenylquinone derivatives formed by oxidation of substituted hydroquinone ethers. *Helvetica Chimica Acta* **1948**, *31*, 525-535. d) Liebeskind, L. S.; Riesinger, S. W. Palladium-catalyzed oxidative dimerization of stannylquinones. A simple method for the synthesis of symmetrical 2,2'-bisquinones. *Tetrahedron Letters* **1991**, *32*, 5681-5682. e) Musgrave, O. C. The Oxidation of Alkyl Aryl Ethers. *Chemical Reviews* **1969**, *69*, 499-531; f) Giza, Y.-H. C.; Kun, K. A.; Cassidy, H. G. Electron Exchange Polymers. XVI. The Oxidation Behavior of Dimethyl Ethers of Hydroquinone and Methyl-Substituted Hydroquinones. *Journal of Organic Chemistry* **1962**, *27*, 679-682.

5) Love, B. E.; Bonner-Stewart, J.; Forrest, L. A. Improved Synthesis of Diquinones. *Synlett* **2009**, 813-817.

6) Love, B. E., unpublished results.

7) Zaytsev, A. V.; Anderson, R. J.; Bedernjak, A.; Groundwater, P. W.; Huang, Y.; Perry, J. D.; Orenga, S.; Roger-Dalbert, C.; James, A. Synthesis and testing of chromogenic phenoxazinone substrates for □-alanyl aminopeptidase. *Organic & Biomolecular Chemistry* **2008**, *6*, 682-692.

8) Owing to the dimeric nature of the diquinone, the mole ratio of quinone:diquinone is not the same as either the weight ratio or yield ratio of these same products.

9) In these reactions, the amount of monoquinone formed was so small (less than 0.01 g in both cases) that small errors in weight determination could easily have had a large effect on calculated mole ratios.

10) Though designated as "quinone-favoring protocols," in some cases use of such reaction conditions still provided the diquinone as the major product.

11) See supplementary data for experimental details.

12) Vitamin K and the ubiquinones are perhaps the best-known examples of such compounds, though embelin, maesaquinone and avarone are also representative members of this class that have biological activity.

13) Examples include biembelin, burmanin A and cuculoquinone. Additionally, diquinones are potential precursors to biologically significant dibenzofuran-1,4-diones such as the anticancer agent popolohuanone E.

Table 1. Oxidation of 2-*tert*-butyl-1,4-dimethoxybenzene by CAN

Entry	Substrate Solvent	CAN Solvent	Mode of Addition	Quinone: Diquinone Mole Ratio	Protocol Designation
1	10.0 mL DMSO	none	Standard	quinone only	**A**
2	10.0 mL DME	none	Standard	quinone only	
3	10.0 mL DMSO	5.0 mL H2O	Standard	48 : 1	**B**
4	14.0 mL THF	7.0 mL H2O	Standard	27 : 1	**C**
5	14.0 mL THF + 1.0 mL DMSO	7.0 mL H2O	Standard	23 : 1	
6	14.0 mL EtOAc	7.0 mL H2O	Standard	10 : 1	
7	2.0 mL DMSO	7.0 mL H2O	Standard	6 : 1	
8	10.0 mL DMSO	5.0 mL H2O	Inverse	6 : 1	
9	7.0 mL THF	7.0 mL H2O + 7.0 mL THF	Inverse	5 : 1	
10	14.0 mL THF	7.0 mL H2O	Inverse	5 : 1	
11	21.0 mL acetone + 7.0 mL H2O	14.0 mL H2O	Standard	4 : 1	
12	14.0 mL CH3CN	7.0 mL H2O	Standard	2.8 : 1	
13	3.5 mL THF	3.5 mL H2O	Inverse	2.7 : 1	
14	1.0 mL THF	3.5 mL H2O	Standard	2.5 : 1	
15	7.0 mL CH3CN	7.0 mL H2O	Standard	2.3 : 1	**Traditional**
16	3.5 mL CH3CN	7.0 mL H2O	Inverse	1.7 : 1	
17	2.0 mL THF	7.0 mL H2O	Inverse	1.7 : 1	
18	2.0 mL CH3CN	3.5 mL H2O	Standard	1.6 : 1	
19	4.0 mL CH3CN	7.0 mL H2O	Inverse	1.5 : 1	
20	1.0 mL THF	3.5 mL H2O	Inverse	1.2 : 1	**D**
21	3.5 mL CH3CN	3.5 mL H2O	Inverse	1 : 1	
22	2.0 mL DMSO	7.0 mL H2O	Inverse	1 : 1	
23	2.0 mL CH3CN	3.5 mL H2O	Inverse	1 : 1.3	**E**
24	7.0 mL CH3CN	7.0 mL H2O	Inverse	1 : 1.9	**F**

Table 2. Oxidation of 2,5-dimethoxytoluene by CAN

Entry	Substrate Solvent	CAN Solvent	Mode of Addition	Quinone: Diquinone Mole Ratio	Protocol Designation
1	10.0 mL DMSO	none	Standard	20 : 1	**A**
2	10.0 mL DME	none	Standard	10 : 1	
3	10.0 mL DMSO	5.0 mL H2O	Standard	4 : 1	**B**
4	10.0 mL DMSO	5.0 mL H2O	Inverse	1.2 : 1	
5	14.0 mL THF	7.0 mL H2O	Standard	1 : 2.4	**C**
6	10.0 mL THF	14.0 mL H2O	Standard	1 : 4	
7	2.0 mL DMSO	7.0 mL H2O	Standard	1 : 6	
8	14.0 mL THF	7.0 mL H2O	Inverse	1 : 7	
9	14.0 mL EtOAc	7.0 mL H2O	Standard	1 : 9	
10	1.0 mL THF	3.5 mL H2O	Standard	1 : 12	
11	7.0 mL CH3CN	7.0 mL H2O	Standard	1 : 14	**Traditional**
12	2.0 mL DMSO	7.0 mL H2O	Inverse	1 : 14	
13	2.0 mL CH3CN	3.5 mL H2O	Inverse	1 : 18	**E**
14	1.0 mL THF	3.5 mL H2O	Inverse	1 : 20	**D**
15	7.0 mL CH3CN	7.0 mL H2O	Inverse	1 : 22	**F**
16	2.0 mL CH3CN	3.5 mL H2O	Standard	1 : 58	

Table 3. Oxidation of 2-alkyl-1,4-dimethoxybenzene derivatives by CAN

	Quinone-Favoring Protocols			*Traditional Protocol*			*Diquinone-Favoring Protocols*		
R	**Protocol Used**	**Yield of 2 (%)**	**2 : 3 Mole Ratio**	**Yield of 2 (%)**	**2 : 3 Mole Ratio**	**Yield of 3 (%)**	**2 : 3 Mole Ratio**	**Yield of 3 (%)**	**Protocol Used**
Me	A	72	20 : 1	3	1 : 14	89	1 : 20	82	D
Me	B	42	4 : 1				1 : 18	90	E
Me	C	12	1 : 2.4				1 : 22	93	F
Et	B	63	17 : 1	8	1 : 4.7	73	diquinone only	84	E
Et	C	18	1 : 1				1 : 20	75	F
n-Pr	A	80	> 50 : 1	20	1 : 1.7	67	1 : 3.9	77	E
n-Pr	B	63	19 : 1						
n-Pr	C	20	1 : 1.2						
n-Bu	B	58	13 : 1	17	1 : 1.9	64	1 : 6.1	78	F
n-Bu	C	35	2.6 : 1						
i-Bu	B	68	30 : 1	17	1 : 1.9	67	1 : 3.1	76	F
i-Bu	C	36	2 : 1						
t-Bu	A	70	> 50 : 1	42	2.3 : 1	37	1.2 : 1	55	D
t-Bu	B	73	48 : 1				1 : 1.3	55	E
t-Bu	C	82	27 : 1				1 : 1.9	46	F
n-pentyl	A	70	> 50 : 1	14	1 : 2.4	65	1 : 12	80	E
n-pentyl	B	63	12 : 1						
n-pentyl	C	25	1 : 1						
n-heptyl	B	51	14 : 1	12	1 : 2.4	59	1 : 4.4	64	E
n-heptyl	C	33	2.3 : 1				1 : 19	93	F
n-nonyl	B	28	26 : 1	22	1: 1.3	57	1 : 3.8	73	E
n-nonyl	C	32	3.3 : 1				1 : 2.9	69	F
n-undecyl	C	39	2.3 : 1	21	1 : 1.8	75	1 : 63	96	D

(Figure for Table 3)