Synthesis and Oxidizing Ability of *p*-Chloranil Dimer

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A *p*-chloranil dimer (pCh_2) has been synthesized. The first reduction potential of pCh_2 shifted to a more positive value than that observed for the *p*-chloranil monomer (pCh_1) and was more negative than that for 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). As expected, pCh_2 oxidized 9,10-dihydroanthracene and α -tetralol to give anthracene and α -tetralone, respectively, more efficiently than pCh_1 did. The advantages of pCh_2 were observed in oxidations of 2,4-di-*tert*-butylphenol and 2,6-di-*tert*butyl-4-methylphenol. Although further oxidation took place in DDQ oxidations and no reaction occurred in pCh_1 oxidations, initial oxidation products were solely obtained in pCh_2 oxidation because of its moderate oxidizing ability.

Ouinones are widely used as organic oxidizing agents.¹ Typically, they are employed in the dehydrogenation of hydroaromatic compounds² and chromanones,³ oxidation of allyl⁴ and benzyl alcohols to aldehydes or ketones,5 oxidation of the benzylic position to give alcohols,⁶ oxidative cyclization,⁷ and oxidative coupling of phenolic compounds.⁸ Unique reactivity has been seen in some of these reactions. Among various quinonoid oxidizing agents, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and tetrachloro-p-benzoquinone (p-chloranil, pCh_1) are most frequently used. DDQ has a strong oxidizing ability; however, it decomposes to generate highly toxic hydrogen cyanide gas in the presence of water or alcohols. In this respect, p-chloranil is advantageous because it produces no hydrogen cyanide; however, its oxidizing ability is rather low. The relative reaction rates of the dehydration of 1.2-dihydroanthracene by DDQ and p-chloranil have been reported to be approximately 5500:1.9 We have designed a new oxidizing agent, a p-chloranil dimer (pCh₂). Like pCh₁, pCh₂ does not generate hydrogen cyanide. In addition, the dimer structure may give rise to higher oxidizing ability than that of pCh_1 . It is well known that the oxidizing ability of a quinonoid compound depends on its ability to withdraw an electron from the substrate or to abstract a hydride ion.¹⁰ Both should be significant in pCh_2 because the resulting radical anion 1 or anion 2 would be highly stabilized by the electron-withdrawing character of the quinonoid substituent (Figure 1). Previously, we reported a significant positive shift of the reduction potentials of benzoquinone dimers compared with those of their monomers.¹¹ In the present article, the synthesis and reduction potential of pCh_2 and its behavior as an oxidizing agent in some reactions are described and compared with those of pCh_1 and DDQ.

 pCh_2 was synthesized as shown in Figure 2. *p*-Dimethoxybenzene dimer **3** was perchlorinated¹² using sulfuryl chloride in the presence of diisopropylamine to give **4**. As direct oxidation using cerium(IV) ammonium nitrate (CAN) failed, **4** was demethylated to hydroquinone dimer **5** using BBr₃, and then oxidized by CAN to afford **1** in good yield. The obtained pCh_2 was identified by ¹³CNMR, MS, IR, and elemental analyses.¹³

Table 1. Half-wave reduction potentials for pCh_1 , pCh_2 , and DDQ^a

Compd	E_1/V	E_2/V	E_3/V
pCh ₁ pCh ₂	+0.03 (1e) +0.13 (1e)	-0.71 (1e) -0.11 (1e)	-1.08 (2e)
DDQ	+0.54 (1e)	-0.27 (1e)	

^aElectrode; Pt (working), Pt (counter), and SCE (reference). Supporting electrolyte; n-Bu₄NClO₄. Solvent; CH₃CN. Scan rate: 100 mV s⁻¹.



Figure 1. Reduction and hydride abstraction of *p*Ch₂.



Figure 2. Synthesis of *p*Ch₂.

Entry	Substrate	Oxidizing agent	Condition ^b	Conversion /%	Products and Yields /%
1		<i>p</i> Ch ₁	А	9	
2	9,10-dihydroanthracene 9,10-dihydroanthracene	<i>p</i> Ch ₂	A	38	anthracene (100) anthracene (100)
3	9,10-dinydroanthracene OH	DDQ	A	69	o
4		<i>p</i> Ch ₁	В	2	
5	α -tetralol α -tetralol	<i>p</i> Ch ₂	В	10	α -tetralone (100) α -tetralone (100)
6	α -tetralol	DDQ	В	88	α -tetralone (100)
7	→ OH	<i>p</i> Ch ₁	С	0	_
8	6 6	pCh ₂	С	36	OH OH OH CI T (50) 10 (50)
9	6	DDQ	С	100	СН ₃ ССН ₃ СОСН
10	CH ₃	<i>p</i> Ch ₁	D	0	_
	2				UH K
11	BHT	pCh ₂	D	20	CH ₂ OCH ₃
12	BHT	pCh ₂	Е	60	12 (100) 12 (100)
13	BHT	DDQ	D	100	СНО 11 (100)

Table 2. Oxidation using pCh_1 , pCh_2 , and DDQ as oxidizing agents^a

^aConversions and yields were based on the ¹HNMR spectra. ^bReactions were performed by the literature methods except E. A (ref 2b): the substrate:quinone = 1:1, in 1,4-dioxane, ambient temperature, 1 h; B (ref 9): the substrate:quinone = 1:1, in methanol, ambient temperature, 30 min; C (ref 14): the substrate:quinone = 4:1, no solvent, 200–230 °C, 5 min; D (ref 8): the substrate:quinone = 1:2, in methanol, ambient temperature, 24 h; E: the substrate:quinone = 1:2, in methanol, 45 °C, 24 h.

The reduction behavior of pCh_2 was examined using cyclic voltammetry (Table 1). pCh_2 showed three reversible waves in acetonitrile, which could be attributed to one-, one-, and two-electron reductions. The first reduction potential (E_1) of pCh_2 shifted to a more positive value by 0.10 V compared with that observed for pCh_1 , but it was more negative than that for

DDQ. Compared with 5,5'-di-*tert*-butyl-2,2'-bi-*p*-benzoquionone (quinone dimer), whose first reduction shifted to a more positive value than that of 2,5-di-*tert*-butyl-*p*-benzoquinone (monomer) by 0.36 V in CH₂Cl₂,^{11a} the effect of dimerization of the perchlorinated quinone was unexpectedly small. This could be because of the large dihedral angle between the two quinone planes, giving little electronic communication between the π systems. In fact, B3LYP/6-31G(d,p) calculations revealed that the dihedral angle was 84° [for (Cl–)C–C–C–C(–Cl)] at the energy minimum as a result of steric repulsion between (C–)Cl and (C=)O atoms at the 1(3) and 1'(3') positions. This indicates that the negative charge in 1 should be localized in half of the molecule, as depicted in Figure 1, and the other half essentially exerts an inductive effect. The hypothesis is further supported by a small gap between E_1 and E_2 in pCh_2 (0.24 V) compared with those in pCh_1 (0.74 V) and DDQ (0.81 V). The second reduction of pCh_2 should proceed in a facile manner because it is virtually the reduction of the quinone moiety of 1, whereas in those of pCh_1 and DDQ, the radical anions undergo reductions, which occur less easily as a result of the on-site Coulomb repulsion.

The oxidizing ability of pCh_2 was investigated. Since the purpose of this article is to compare pCh_2 with pCh_1 and DDQ, the reactions were conducted using literature methods, as noted in Table 2 and, except for Entry 12, were not optimized. Dehydrogenation of 9,10-dihydroanthracene at ambient temperature^{2b} yielded anthracene as the sole product in all cases (Entries 1–3). The conversion of the pCh_2 oxidation was between those of the DDQ and pCh_1 oxidations, as expected from the order of the first reduction potentials E_1 . Similar results were obtained in the oxidation of α -tetralol, giving α -tetralone in methanol (Entries 4–6).⁵ Note that DDQ showed high reactivity but gradually decomposed to generate hydrogen cyanide gas under the present conditions, whereas the reactivity of *p*-chloranil was too low. In such a case, pCh_2 may be a better choice with respect to safety and efficiency.

Next, oxidation of 2,4-di-*tert*-butylphenol (6) was examined. In DDQ oxidation, 6 is known to undergo oxidative coupling to give 2,2'-biphenol derivative 7 and is then further oxidized to yield furan derivatives 8 and 9 (Entry 9).¹⁴ However, because of its low oxidizing ability, the *p*Ch₁ oxidation did not yield any oxidative products (Entry 7). In contrast, when *p*Ch₂ was used as the oxidizing agent, 7 and 10 were afforded in a 1:1 molar ratio (Entry 8). This can be rationalized in terms of the enhanced oxidizing ability of *p*Ch₂, which facilitated oxidative coupling of 6, and its weaker oxidizing ability compared to that of DDQ, which depressed further oxidation of 7 and 10. A chlorine atom of 10 should originate from 1. Although 10 is known to undergo oxidative coupling by K₃[Fe(CN)₆] to give bis(cyclohexadienone),¹⁵ this reaction was also depressed in the *p*Ch₂ oxidation.

Similarly, 2,6-di-tert-butyl-4-methylphenol (BHT) is reported to give aldehyde 11 quantitatively in DDQ oxidation at ambient temperature (Entry 13).8 In contrast, no reaction took place in the *p*Ch₁ oxidation (Entry 10). Unlike DDQ and *p*Ch₁, using pCh_2 as the oxidizing agent yielded 12 as the sole product, with 20% conversion (Entry 11). When the reaction temperature was increased (45 °C), the conversion increased to 60% (Entry 12). Note that 12 is an intermediate product to give 11 in the DDQ oxidation. Both BHT and 12 undergo one-electron oxidation in the DDQ oxidation,⁸ and should also do so in the pCh_2 oxidation. However, 12 was hardly oxidized in the latter case. This is because the methoxymethyl group behaves as a weakly electron-withdrawing group [the Hammett constant ($\sigma_{\rm p}$) is $+0.01^{16}$] because of the large electronegativity of the oxygen atom, whereas the methyl group is a moderately electrondonating group (-0.17), so it was more difficult for 12 to undergo one-electron oxidation than it was for BHT. The unique reactivity of pCh_2 in this reaction is again attributed to its moderate oxidizing ability.

In summary, the *p*-chloranil dimer pCh_2 was synthesized from dimethoxybenzene dimer 3 in good yield. Since the first reduction potentials were found to be more negative in the order pCh₁, pCh₂, and DDO, the yields of the oxidation of 9,10dihydroanthracene and α -tetralol to give anthracene and α tetralone, respectively, increased in this order. In contrast, oxidations of 2,4-di-tert-butylphenol and BHT yielded different products when pCh_2 was used as the oxidizing agent instead of DDQ. This is thought to be because no further reaction occurred in the *p*Ch₂ oxidation as it is a less strong oxidizing agent than DDQ. Apparently, pCh₂ is a safe and moderately strong oxidizing agent and is thus suitable for reactions where a rather strong oxidizing agent is required but further oxidation should be avoided. Further investigations of the oxidizing ability of pCh_2 , including optimization of the reaction conditions, are currently underway.

References and Notes

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- 12 Readers who are obscurely anxious about the toxicity of polychlorinated compounds should read the following book. IUPAC White Book of Chlorine as *Pure and Applied Chemistry*, **1996**, Vol. 68.
- 13 Compound 1: ¹³C NMR (150 MHz, CDCl₃): 172.66, 169.95, 143.49, 141.58, 141.18, 135.85. MS (EI): m/z 418 (M⁺), 420 ([M + 2]⁺), 422 ([M + 4]⁺), 424 ([M + 6]⁺), 426 ([M + 8]⁺), 428 ([M + 10]⁺), 430 ([M + 12]⁺). IR (Nujol): v_{max} 1671 cm⁻¹ (C=O). Anal. Calcd for C₁₂O₄Cl₆: C, 34.23%. Found: C, 34.11%.
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