(D_2O) δ 2.35-2.65 (m, 8 H, CH_2CH_2), 6.95 (s, 2 H, CH=CH), 7.3-7.6 (m, 4 H, Ar).

Registry No. **1a**, 90549-82-9; **1b**, 76673-34-2; **1c**, 97860-58-7; **1d**, 118071-16-2; **2a**, 118111-04-9; **2b**, 76673-35-3; **2c**, 97860-59-8; O_2, 7782-44-7.

Facile and Convenient Syntheses of Quinones from Phenols

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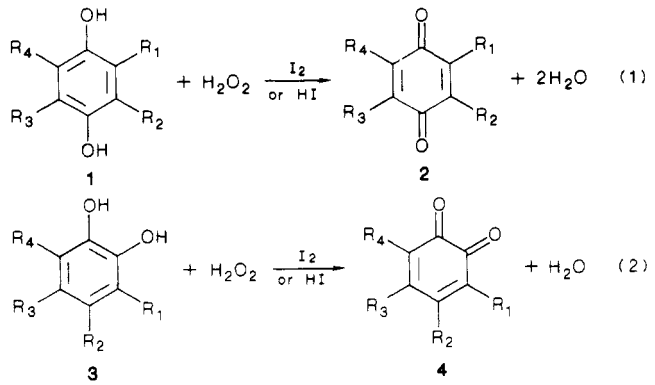
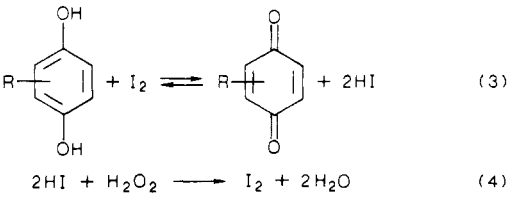
The oxidation of monohydroxy and dihydroxy aromatics is the most general method to obtain quinones. The oxidation of 1,2- or 1,4-dihydroxybenzenes to the corresponding quinones has been achieved by a variety of oxidants. The use of silver oxide or silver carbonate is generally the method of choice,[1] but it is not practical for large-scale preparations, due to the expensive oxidants.

Recently, a new method of oxidation of 1,4-hydroquinones to 1,4-benzoquinones by diphenyl diselenide catalyzed hydrogen peroxide has been reported.[2] That prompts up to report a patented,[3] new facile, general procedure of oxidation of dihydroxybenzenes, which is more convenient and less expensive than the methods so far known. The procedure involves the oxidation of the dihydroxybenzenes by H_2O_2 in methanolic or aqueous solution, depending on the solubility of the dihydroxybenzene, at room temperature in the presence of catalytic amounts of I_2 or HI (eq 1 and 2). While the reaction is

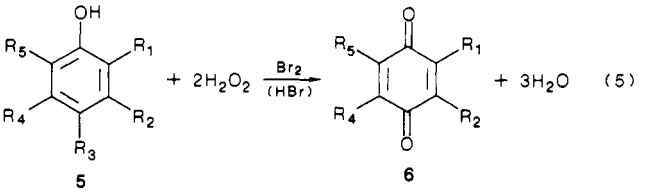


also catalyzed by Br_2, it is less selective because of the competitive electrophilic addition of bromine to the activated aromatic ring, and with complete conversions of the dihydroxybenzenes the yields are generally significantly lower (Table I) compared with I_2 catalysis. Chlorine is not suitable.

The actual oxidant appears to be I_2 (eq 3) and hydrogen peroxide serves to regenerate iodine from HI (eq 4). In the absence of iodine the starting dihydroxybenzene is recovered unchanged. However, the use of a stoichiometric amount of iodine leads only to low conversions (~10%) of the dihydroxybenzene to the quinone. On the other hand, the quinone is significantly reduced to hydroquinone by HI, clearly indicating that reaction of eq 3 is reversible and the equilibrium is shifted at left. Our procedure is particularly effective because the fast oxidation of HI by H_2O_2 (eq 4) keeps very low the stationary concentration of HI, shifting the equilibrium of eq 3 at right. Thus hydrogen peroxide makes catalytic in I_2 the process and at the same time makes very efficient the overall reaction by fast oxidation of HI.



The oxidation of monohydric phenols is another general method to obtain *p*-quinones.[1] High yields can be obtained by suitable choice of the oxidant[1] or anodic oxidation.[10] However, severe limitations exist for a large-scale application of the known procedures, also with the most selective and mild oxidants (thallium nitrate,[11] Jones reagent,[12] Fremy's salt,[4] etc.), owing to their toxicity and the high cost. More convenient oxidants, such as molecular oxygen[13] and hydrogen peroxide,[14] have therefore attracted considerable attention; they were generally used in the presence of expensive metal-complex catalysts with moderate to good selectivity and were mainly applied to simple substrates. We now report a new highly selective synthesis of *p*-quinones from 2,6-disubstituted phenols suitable for large-scale work.[3] It involves the oxidation of the phenol by hydrogen peroxide in the presence of molecular bromine or hydrogen bromide as catalyst (eq 5). Also in this case the actual oxidant appears to be bromine (eq 6), and H_2O_2



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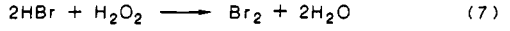
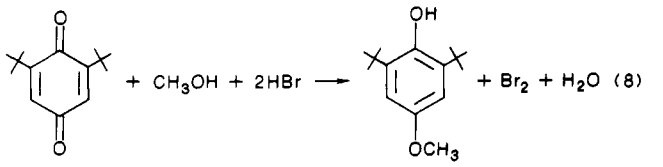


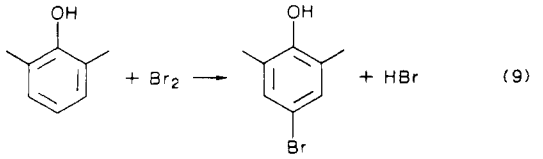
(7)

serves to regenerate Br_2 from HBr (eq 7). The oxidation, in fact, takes place by using stoichiometric amount of bromine under the same conditions, but again the efficiency is much lower because it is known[15] that 2,6-di-*tert*-butyl-*p*-benzoquinone reacts with HBr in methanolic solution giving the 4-methoxy-2,6-di-*tert*-butylphenol (eq 8) and other unidentified compounds containing methoxy



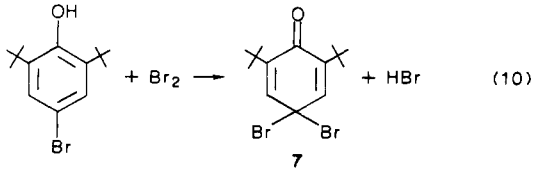
(8)

groups. In the oxidation by stoichiometric Br_2, certainly the first step of the mechanism involves the electrophilic bromination of the phenol (eq 9). On the other hand, it



(9)

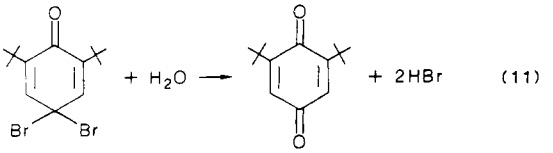
is known[16] that 2,6-di-*tert*-butyl-4-substituted-phenols react with bromine, giving the 2-bromo-4-substituted-2,6-di-*tert*-butyl-3,5-cyclohexadienone or the 4-bromo-4-substituted-2,6-di-*tert*-butyl-2,5-cyclohexadienone, depending on the nature of the substituent in position 4. In particular, the 4-bromo-2,6-di-*tert*-butylphenol gives[16] in high yield the 4,4-dibromo-2,6-di-*tert*-butyl-2,5-cyclohexadienone (eq 10). Actually we have isolated the com-



(10)

7

pound **7** in the initial stage of the bromine-catalyzed oxidation of 2,6-di-*tert*-butylphenol and hydrolyzed it to the corresponding quinone (eq 11). The hydrolysis of **7** to the



(11)

quinone in the presence of H_2O_2 is practically quantitative, but yields are lower in the absence of H_2O_2, probably owing to the side reactions with HBr (eq 8), contributing to explain the lower yields obtained in the oxidation with stoichiometric bromine compared with the bromine-catalyzed oxidation with H_2O_2.

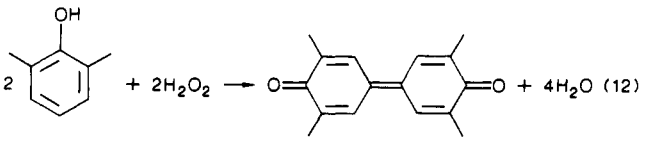
Thus the overall mechanism appears to involve eq 9–11 and 7. Again, as for the oxidation of dihydroxybenzenes with I_2, hydrogen peroxide has a 2-fold function: (i) it makes catalytic in Br_2 the process by fast oxidation of HBr, and (ii) it makes more selective the overall process compared with the use of stoichiometric amount of Br_2 by keeping very low the stationary concentration of HBr.

With iodine, under the same conditions, the yields are significantly lower, probably because the bulky iodine atom makes less favorable the ipso attack. With chlorine only traces of quinones were observed.

Two synthetic procedures have been developed in agreement with this mechanism, which requires that all the phenol must be transformed into the 4-bromo derivative in the initial step because the bromination of the phenol is much faster than the further bromination of the 4-bromophenol. The first procedure involves the use of 0.55 mol of bromine and 2 mol of hydrogen peroxide for mole of phenol in order to make still available a small excess of bromine when all the phenol is transformed in the 4-bromo derivative. In the second procedure 0.1 mol of bromine and 2.5 mol of hydrogen peroxide are used per mole of phenol, but this last is added dropwise within 1 h to the reacting mixture: the fast oxidation of the phenol to the quinone keeps the stationary concentration of the phenol lower than that of bromine, which is continuously regenerated from HBr by H_2O_2 (eq 7). Hydrogen bromide can be utilized instead of Br_2, but an additional 0.5 mol of H_2O_2 must be used per mole of HBr.

Evidently the mechanism (eq 9–11) indicates that the oxidation also occurs with phenols substituted in the para position by a halogen atom (Cl, Br, I). This is clearly shown by the results obtained with the substrates **5g** and **5h** in Table II in which the results are summarized.

Small amounts of dimeric quinones are generally observed as byproducts (eq 12). The high yields, the simple and mild experimental conditions, the generality, and the unexpensive reagents and catalyst recommend these procedures as valuable methods also for industrial applications.[3]



(12)

Experimental Section

General Procedures for the Oxidation of 1 and 3 (eq 1, 2). (**A**) H_2O_2 (60%) (10.0 mL, 0.22 mol) was added dropwise with stirring to a solution of dihydroxybenzene (0.20 mol), I_2 (10 mmol), and concentrated H_2SO_4 (10 mL) in methanol (600 mL) at room temperature. After 4 h part of the formed quinone crystallized and was collected by filtration. The methanolic solution was poured in 100 mL of water and extracted with ether, and the quinones were purified by flash chromatography on silica gel (hexane–ethyl acetate, 3:1). The products were identified by the melting points (Table I) and by comparison of the IR and NMR spectra of authentic samples.

(**B**) A procedure similar to A has been utilized with dihydroxybenzenes, which have sufficient solubility in water, such as hydroquinone, 2-methylhydroquinone, and 2,6-dimethylhydroquinone, with the only difference that water was used instead of methanol. In this way the quinone directly crystallized from the aqueous solution and was easily separated by simple filtration.

(**C**) A procedure similar to A was followed with the difference that 20 mmol of HI was utilized instead of I_2.

(**D**) A procedure similar to B was followed with the difference that 20 mmol of HI was utilized instead of I_2.

(**E**) The same procedure as in A was used, with the difference that 10 mmol of Br_2 was utilized instead of I_2.

The results are summarized in Table I.

Procedure B has been utilized with hydroquinone and stoichiometric amount of I_2 in the absence of H_2O_2. The conversion of hydroquinone to *p*-benzoquinone is 10%; most of the hydroquinone is left unchanged.

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Table I. Oxidation of 1,2- and 1,4-Dihydroxybenzenes by H_2O_2

substrate	R_1	R_2	R_3	R_4	product	procedure	yield, %	mp, °C found	mp, °C lit.	(ref)
1a	H	H	H	H	**2a**	A	97	114	115	(4)
1a					**2a**	B	93			
1a					**2a**	C	95			
1a					**2a**	D	93			
1a					**2a**	E	52			
1b	CH_3	H	H	H	**2b**	A	98	68	68–69	(4)
1b					**2b**	B	92			
1b					**2b**	C	94			
1b					**2b**	D	93			
1c	CH_3	H	H	CH_3	**2c**	A	95	72	72–3	(4)
1c	CH_3	H	H	CH_3	**2c**	B	92			
1c					**2c**	C	94			
1c					**2c**	D	92			
1d	CH_3	CH_3	H	CH_3	**2d**	A	98	32	32	(4)
1d					**2d**	D	96			
1d					**2d**	E	94			
1e	CH_3	CH_3	CH_3	CH_3	**2e**	A	92	110	111	(4)
1f	CH_3	H	H	C_2H_5	**2f**	A	87	40	40–1	(4)
1g	t-Bu	H	H	t-Bu	**2g**	A	86	67	67	(5)
1g					**2g**	C	88			
1g					**2g**	E	68			
1h	t-Bu	H	t-Bu	H	**2h**	A	91	152	152	(6)
1i	Ph	H	H	Ph	**2i**	A	97	138	138	(7)
3a	H	CH_3	CH_3	H	**4a**	A	74	102	102	(4)
3b	H	t-Bu	H	H	**4b**	A	72	66	66–7	(6)
3c	t-Bu	H	t-Bu	H	**4c**	A	76	115	114–5	(6)
3c					**4c**	D	75			
3c					**4c**	E	48			
1,4-dihydroxynaphthalene					1,4-naphthoquinone	A	98	124	124	(8)
1,4-dihydroxynaphthalene					1,4-naphthoquinone	D	97			
1,4-dihydroxynaphthalene					1,4-naphthoquinone	E	72			
2-methyl-1,4-dihydroxynaphthalene					2-methyl-1,4-naphthoquinone	A	98	106	107	(9)

Table II. Bromine-Catalyzed Oxidation of Phenol 5 to Quinone 6 by H_2O_2

substrate	R_1	R_2	R_3	R_4	R_5	product	procedure	yield,[a] %	mp, °C found	mp, °C lit.	(ref)
5a	CH_3	H	H	H	CH_3	**6a**	A	85	72	72–73	(4)
5a						**6a**	B	82			
5a						**6a**	C	86			
5a						**6a**	D	83			
5b	CH_3	CH_3	H	H	CH_3	**6b**	A	77	32	32	(4)
5b						**6b**	C	82			
5c	CH_3	CH_3	H	CH_3	CH_3	**6c**	A	92	110	111	(4)
5c						**6c**	C	90			
5d	C_6H_5	H	H	H	C_6H_5	**6d**	A	95	137–8	138	(7)
5d						**6d**	C	92			
5e	CH_3	H	H	H	C_2H_5	**6e**	A	84	40	40	(4)
5f	t-C_4H_9	H	H	H	t-C_4H_9	**6f**	A	97	66–7	67	(5)
5f						**6f**	B	94			
5f						**6f**	C	95			
5f						**6f**	D	91			
5g	t-C_4H_9	H	Cl	H	t-C_4H_9	**6g**	A	98	67	67	(5)
5g						**6g**	C	94			
5h	t-C_4H_9	H	Br	H	t-C_4H_9	**6h**	A	96	66–7	67	(5)
5h						**6h**	C	95			
5i	2-methylnaphthol					**6i**[b]	A	90	107	107	(9)

[a] Based on starting phenol. [b] 2-Methyl-1,4-naphthoquinone.

Reduction of *p*-Benzoquinone by HI. *p*-Benzoquinone reacts with stoichiometric amount of HI under the conditions of procedure B, giving 52% of hydroquinone and 44% of unchanged *p*-benzoquinone.

General Procedures for the Oxidation of 5 (eq 5). Procedure A. The substituted phenol **5** (0.1 mol) and Br_2 (2.83 mL, 0.055 mol) were added to a solution of 60% H_2O_2 (9.8 mL, 0.2 mol) and concentrated H_2SO_4 (6 mL) in methanol (300 mL). The resulting mixture was refluxed for 20 min and then concentrated to 100 mL and cooled at 0 °C; the precipitated quinone **2** was collected by filtration and recrystallized from pentane. Residual amounts of quinone were recovered by dilution of methanolic solution with water, extraction with ether, and isolation by flash chromatography on silica gel (hexane–ethyl acetate, 3:1). The quinones **6** were identified by the melting points and comparison with authentic samples (IR, NMR).

Procedure B. The procedure is similar to A with the difference that HBr (0.11 mol) and H_2O_2 (0.25 mol) were utilized instead of Br_2 (0.055 mol) and H_2O_2 (0.2 mol).

Procedure C. A solution of the phenol **5** (0.1 mol) in methanol (100 mL) was added dropwise within 1 h to a refluxed solution of Br_2 (0.52 mL, 0.01 mol), 60% H_2O_2 (12.2 mL, 0.25 mol), and concentrated H_2SO_4 (6 mL) in methanol (100 mL). The solution was refluxed for additional 5 min and worked up as in A.

Procedure D. The procedure is similar to C with the difference that HBr (0.02 mol) and H_2O_2 (0.27 mol) were used instead of Br_2 (0.01 mol) and H_2O_2 (0.25 mol).

The results are summarized in the Table II.

Procedure A has been utilized by using iodine instead of bromine with **5f**; the yield of **6f** is 16%. Under the same con-

ditions with Cl_2 instead of Br_2 only traces (<2%) of **6f** were observed.

Hydrolysis of the Dibromocyclohexadienone 7. Procedure A at room temperature allows the separation of the dibromocyclohexadienone **7** in 10% yield by flash chromatography on silica gel (hexane–ethyl acetate, 3:1) as a crystalline product: mp 127 °C (lit.[16] mp 127–128 °C); IR 1660 cm^{-1}; ^1H NMR δ 1.2 (s, t-Bu, 18 H), 7.08 (s, CH of quinone, 2 H); MS, m/z 306 (M^+), 284, 269, 253, 242, 252, 189.

Hydrolysis of 7 in the Presence of H_2O_2. The hydrolysis of **7** was performed under the same conditions of procedure A in the absence of Br_2. A quantitative yield of 2,6-di-*tert*-butyl-*p*-benzoquinone was obtained.

Hydrolysis of 7 in the Absence of H_2O_2. The hydrolysis was performed under the same conditions of procedure A by using 10 mL of H_2O instead of H_2O_2 and in the absence of Br_2. A 47% yield of 2,6-di-*tert*-butyl-*p*-benzoquinone was obtained.

Oxidation of 2,6-Di-*tert*-butylphenol by Stoichiometric Br_2. Procedure A was utilized by using a stoichiometric amount of Br_2 and in the absence of H_2O_2. A 37% yield of 2,6-di-*tert*-butyl-*p*-benzoquinone was obtained.

Acknowledgment. The research has been supported by the CNR, Progetto Finalizzato Chimica Fine e Secondaria.

Registry No. **1a**, 123-31-9; **1b**, 95-71-6; **1c**, 654-42-2; **1d**, 700-13-0; **1e**, 527-18-4; **1f**, 72693-14-2; **1g**, 2444-28-2; **1h**, 88-58-4; **1i**, 13379-77-6; **2a**, 106-51-4; **2b**, 553-97-9; **2c**, 137-18-8; **2d**, 935-92-2; **2e**, 527-17-3; **2f**, 29148-36-5; **2g**, 2460-77-7; **2h**, 719-22-2; **2i**, 844-51-9; **3a**, 2785-74-2; **3b**, 98-29-3; **3c**, 1020-31-1; **4a**, 4370-50-7; **4b**, 1129-21-1; **4c**, 3383-21-9; **5a**, 576-26-1; **5b**, 2416-94-6; **5c**, 527-35-5; **5d**, 2432-11-3; **5e**, 1687-64-5; **5f**, 128-39-2; **5g**, 4096-72-4; **5h**, 1139-52-2; **5i**, 7469-77-4; **7**, 1144-36-1; 1,4-dihydroxynaphthalene, 571-60-8; 2-methyl-1,4-dihydroxynaphthalene, 481-85-6; 1,4-naphthaquinone, 130-15-4; 2-methyl-1,4-naphthaquinone, 58-27-5.

Synthesis of 1-Alkyl-1,2,4-triazoles: A New One-Pot Regiospecific Procedure[1]

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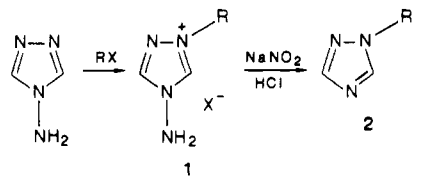
Received September 22, 1988

Regiospecific alkylation of 1,2,4-triazoles provides a synthetic challenge.[2] Direct alkylation of 1,2,4-triazole affords usually a mixture of mainly 1- and some 4-substituted product.[3] Ratios vary with the nature of the alkylating agent and conditions but frequently range from 70:30 to 90:10. Preparation of 1-substituted 1,2,4-triazoles has become important of late, as a number of such triazoles has been found to be very effective agricultural fungicides,[4] antimycotics,[5] and more recently aromatase inhibitors.[6]

Scheme I



4-Amino-1,2,4-triazole (4-AT) is an activated and blocked triazole that can be prepared directly from hydrazine and derivatives of formic acid.[7] We report a regiospecific one-pot synthesis of some 1-alkyl-1,2,4-triazoles based on the alkylation of 4-amino-1,2,4-triazole and the subsequent deamination of the so formed triazolium salt (Scheme I).

Results and Discussion

Alkylation of 4-AT proceeded easily in polar media (isopropyl alcohol, or acetonitrile) exclusively at N-1 usually in good yield (Table I). In the case of alkylation with *sec*-butyl bromide, the yield of **1g** was only 59%, owing to the difficulty encountered in separating **1g** from remaining aminotriazole. However, a satisfactory yield of **2g** was obtained in the one-pot reaction. The aminotriazolium salts (**1a–h**) were deaminated readily with a slight excess of nitrous acid in essentially quantitative yield. Evolution of nitrous oxide was observed during deamination, as has been found in nitrous acid deamination of other 1,1-disubstituted aromatic hydrazines.[8] It should be noted that the 2,4-dichlorophenacyltriazole (**2c**) reacts with nitrous acid at ambient temperature. Therefore, it is advisable to carry out deaminations at 0–5 °C and to avoid too large an excess of nitrous acid.

We found that the alkylation and deamination reactions could be performed sequentially in one-pot in good yield without isolation of the aminotriazolium salts. Alkyltriazole isolation is facilitated by the fact that any 4-AT (starting material) or 1,2,4-triazole (a potential byproduct) remains in the aqueous phase from which the desired product is precipitated or extracted. This reaction sequence is useful for alkylating agents as unreactive as primary alkyl chlorides as well as for more reactive benzylic and phenacyl halides. Furthermore, the mild nonbasic conditions employed here are particularly suited to alkylating agents that bear base-sensitive substituents, which contrast with the strongly basic conditions frequently used in direct alkylations of triazoles. The reaction sequence has failed with trityl chloride, however, because the intermediate trityl(aminotriazolium) salt undergoes solvolysis to form trityl alcohol under the acidic deamination conditions used.

Our work provides the first example of a fairly general high-yield regiospecific one-pot synthesis of 1-substituted 1,2,4-triazoles from 4-AT,[9] although alkylation of 4-AT[10] and deamination of aminotriazoles[11] and -triazolium salts[10]

(1) Dedicated to Dr. Alan R. Katritzky on the occasion of his 60th birthday.

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