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QUINONES—VII[1]

HALOGENATION AND OXIDATIVE HALOGENATION OF PHENOLS WITH HYDROGEN HALIDES/HYDROGEN PEROXIDE. SYNTHESIS OF *p*-CHLORANIL AND *p*-BROMANIL

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Abstract—Chloranil **6** and bromanil **7** are prepared in very good yields from phenol or hydroquinone with concentrated hydrochloric or hydrobromic acid/30% hydrogen peroxide and magnesium chloride as catalyst. With catechol the reaction stops at the tetrachloro- or tetrabromo-*o*-hydroquinone (**4** or **5**) stage. The iodination of phenol with potassium iodide/hydrogen-peroxide in acetic acid yields 2,4,6-tri-iodophenol (**3**).

Hydrogen peroxide oxidizes hydrogen halides (HX, with the exception of hydrogen fluoride) to the halogens[2-6] (reaction 1).

$$H_2O_2 + 2HX \xrightarrow{k'} X_2 + 2H_2O \qquad (1)$$

$$X_2 + H_2O_2 \xrightarrow{k''} O_2 + 2HX \qquad (2)$$

$$X = Cl, Br, I$$

This reaction has already been used for the *in situ* generation of halogens in the synthesis of chloro-, bromo- and iodo-hydrines or 1,2-dichloroalkanes from alkenes,[7-9] in the chlorination of ketones,[10] in the chlorination and bromination of substituted anilines,[11] hydroxybenzoic acids[12] and hydroxyquinolins,[13] in the chlorination of 3-aminopyridine,[14] arylisoxazoles,[15] 2-methylbenzimidazole[16] and octaethylporphyrine,[17] in the bromination of nitrophenol,[18] perylene[19] and bisphenol A[7] and the iodination of pyrrole.[20] 2,3,5-Trialkyl-phenols with iodine/hydrogen peroxide yield 2,3,5-trialkyl-6-iodo-benzoquinones.[21]

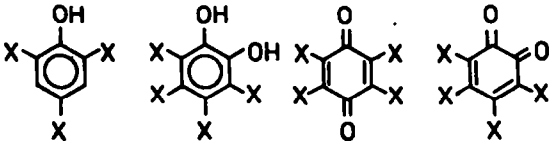
We describe experiments on the halogenation of phenol† and on the preparation of *o*- and *p*-chloranil and *o*- and *p*-bromanil from phenol or catechol and hydrogen peroxide/HX.[23] This method is of potential interest with respect to pollution free production of halophenols and the haloanils.

In aqueous solution the halogens are liable to oxidize hydrogen peroxide (reaction 2).[2-6] The rate constants of reactions 1 and 2 are of comparable magnitude, but the ratio k'/k'' and hence the steady-state concentration of X_2 increases with the decreasing amount of water in the reaction mixture.[24]‡ The values of $[Cl_2 + Cl_3^{\ominus}]$ at 25°C are, e.g. in 2.84 M HCl: 1×10^{-6} mol/l and in 5.25 M HCl: 7×10^{-4} mol/l[25] (with small concentrations of hydrogen peroxide in both cases).[25] Moreover raising the concentration of HX is more effective than raising the hydrogen peroxide concentration.[2] The reason is, that undissociated HX is involved in reaction (1).[6] Hence we performed the chlorinations and brominations with concentrated hydrogen chloride or hydrogen bromide and 30% hydrogen peroxide.

Employing 85% hydrogen peroxide gave no better results. As we found, the yields could be raised or the amount of hydrogen peroxide diminished by adding magnesium chloride as a catalyst. This is probably due to an effect of the magnesium cation.[4]

As can be seen from the table, chlorination and bromination of phenol, hydroquinone and catechol is possible with nearly stoichiometric amounts of hydrogen peroxide. Apparently the fast halogenation of the phenols competes effectively with reaction (2).

In contrast chlorination of **1** to **10**, an intermediate in the preparation of chloranil from phenol, proceeds slowly.[26] In this case more hydrogen peroxide is lost by reaction (2). Similar conclusions can be drawn in the case of the preparation of bromanil **7**. Chloranil can be prepared without isolating **1** in an one-pot process. Starting with phenol we obtained the best results (97% yield of chloranil) in 40 hr (100°C) with a fourfold molar excess of hydrogen peroxide and with magnesium chloride as a catalyst. The one-pot preparation of bromanil **7** needed a twofold molar excess of hydrogen peroxide. The magnesium chloride catalysed oxidative chlorination and bromination of hydroquinone, yielding **6** or **7**, is again a rapid process and only a small excess of hydrogen peroxide is needed. With catechol the reaction stops mainly at the stage of the tetrachloro- or tetrabromo-*o*-hydroquinones **4** and **5** even using a great excess of hydrogen peroxide. The great excess of hydrogen peroxide needed in the iodination of phenol may be caused by the low concentration of free hydrogen iodide in the reaction mixture (slow reaction 1) and by slow iodination

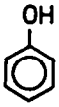
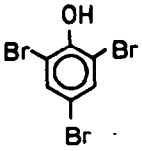
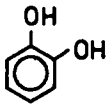


Cl	**1**	**4**	**6**	**8**
Br	**2**	**5**	**7**	**9**
I	**3**			

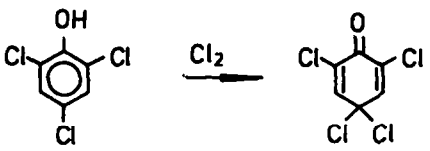
†An early note about the preparation of 2,4,6-trihalophenol from phenol in a similar way contains no experimental data.[22]

‡It should be mentioned that the mechanism of reaction (2) is complicated and k'' represents only an apparent rate constant. Postulated intermediates, e.g. for X = Cl are HOCl[3,5] or HOOCl.[24]

Table 1. Halogenation and oxidative halogenation of phenols with hydrogen halides (HX)/hydrogen peroxide

Phenol	HX	Factor for H_2O_2 [a]	Product	Yield (%)
	HCl	1.3	1	99 [23]
	HCl	4.7	6	97
	HBr	1.3	2	97
	HBr	3.0	7	88 [b]
	HJ	2.7	3	99
	HBr	7.3 [b]	7	98
	HCl	1.2	6	88 [23]
	HBr	1.2	7	94
	HCl	1.0	8	19
	HCl	1.1	4	99
	HBr	1.1	5	73

[a] The factor for the stoichiometric needed amount being 1.0.
[b] Reaction conditions not varied.



1 10

of phenol in comparison to the chlorination and bromination.

EXPERIMENTAL

Chloranil 6 *from phenol.* Hydrogen peroxide (30%, 12 ml, 0.12 mol) was added dropwise to a solution of magnesium chloride hexahydrate (27 g, 0.014 mol) and phenol (1.7 g, 0.018 mol) in conc. hydrochloric acid (270 ml). After raising the temp. (100°C) further hydrogen peroxide (30%, 38 ml, 0.38 mol) was added in four portions at intervals of 8 hr. Stirring was continued for 8 hr at 100°C. After filtration, washing (methanol) and drying we obtained 4.3 g (97%) 6. Identification by m.p. 288°C (lit.[27] 290°C), IR and UV spectra.

Chloranil 6 *from hydroquinone.* Hydrogen peroxide (30 ml, 0.3 mol) was added within 15 min to a stirred, ice-cooled mixture of hydroquinone (5.5 g, 0.05 mol), magnesium chloride hexahydrate (35 g, 0.17 mol) and conc. hydrochloric acid (400 ml). After heating to 95°C for 2 hr, filtration and drying we obtained 10.8 g (88%) 6. Identification as above.

o-*Chloranil* 8. Hydrogen peroxide (30%, 25 ml, 0.25 mol) was added dropwise to an ice-cooled solution of catechol (5.5 g, 0.05 mol) in conc. hydrochloric acid (200 ml). After keeping at 45°C for 2 hr, the filtrate was extracted with chloroform. After crystallization from glacial acetic acid the evaporation residue of the extract yielded 1.5 g (18.5%) 8 with a m.p. 133°C (lit.[28a] 133°C). Identification by IR and UV spectra.

3,4,5,6-*Tetrachlorocatechol* 4. Hydrogen peroxide (30%, 16 ml, 0.16 mol) was added within 2 hr at 0–10°C to a mixture of catechol (4 g, 0.036 mol), glacial acetic acid (40 ml), and conc. hydrochloric acid (220 ml). After filtration, washing and drying we obtained 8.7 g (99%) 4. M.p. 194°C (from glacial acetic acid, lit.[28a] 194°C). Identification by IR and UV spectra.

2,4,6-*Tribromophenol* 2. Hydrogen peroxide (30%, 40 ml, 0.4 mol) was added dropwise to an ice-cooled solution of phenol (9.6 g, 0.1 mol) in conc. hydrobromic acid (150 ml). The mixture was stirred at 60°C for 4 hr. After filtration, washing and drying the yield of 2 was 32.7 g; m.p. 91–93°C (lit.[27] 93.2–93.3°C). Identification by ^{1}H-NMR and IR spectra.

Bromanil 7 *from hydroquinone.* Hydrogen peroxide (30%, 20 ml, 0.2 mol) was added dropwise to a mixture of hydroquinone (4.0 g, 0.036 mol), magnesium chloride hexahydrate (10.0 g, 0.05 mol) and conc. hydrobromic acid (200 ml). After stirring for 3 hr at 100°C filtration, washing and drying gave 14.5 g (94%) 7, m.p. 298°C (from toluene, lit.[28b] 300°C). IR(KBr): 1670 (CO), 1545 cm^{-1} (C=C).

Bromanil 7 *from phenol.* Hydrogen peroxide (30%, 12 ml, 0.12 mol) was added slowly to phenol (1.9 g, 0.02 mol) and magnesium chloride hexahydrate (15.0 g, 0.065 mol) in conc. hydrobromic acid (200 ml). After stirring at 100°C for 24 hr further 24 ml (0.24 mol) of 30% hydrogen peroxide were added in three portions at intervals of 6 hr. Cooling, filtration, washing, and drying yielded 6.0 g (81%) bromanil. Identification as above. No optimum reaction conditions were determined.

Bromanil 7 *from* 2. Hydrogen peroxide (30%, 15 ml, 0.15 mol) was added dropwise to a mixture of magnesium chloride hexahydrate (10.6 g, 0.05 mol), 2 (6.0 g, 0.018 mol) and conc. hydrobromic acid (270 ml). The temp. was then raised to 100°C. At intervals of 6 hr further 25 ml (0.25 mol) of 30% hydrogen perox-

ide were added in two portions. After keeping 5 hr at 100°C, filtration, washing, and drying the yield of 7 was 7.5 g (98%). Identification as above.

3,4,5,6-Tetrabromocatechol 5. Within 30 min at 0–10°C hydrogen peroxide (30%, 16 ml, 0.16 mol) was added dropwise to a stirred mixture of catechol (4.0 g, 0.036 mol), glacial acetic acid (40 ml) and conc. hydrobromic acid (220 ml), stirring was continued for 2 hr. After filtration, washing, and drying we obtained 11.0 g (73%) 5; m.p. 190°C (from glacial acetic acid, lit.[27] 192–193°C). Identification by IR spectrum.

2,4,6-Triiodophenol 3. Hydrogen peroxide (30%, 12 ml, 0.12 mol) was added dropwise to an ice-cooled mixture of phenol (2.4 g, 0.025 mol) and potassium iodide (26.0 g, 0.15 mol) in glacial acetic acid (70 ml). After raising the temperature to 50–60°C further 14 ml (0.14 mol) of 30% hydrogen peroxide were added in two portions at intervals of 2 hr. After stirring 5 hr at 50°C, filtration and washing with aqueous sodium thiosulfate and crystallization from benzene we obtained 11.7 g (99%) 3. M.p. 157°C (lit.[27] 157°C). Identification by IR and ^{1}H-NMR spectra.

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