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Halogenation of Aromatic Compounds by using Sodium Perborate as an Oxidant†

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A facile method for the halogenation of benzene and its derivatives by aqueous haloacids (HCl and HBr) using sodium perborate as an oxidising agent in the presence of tertabutylammonium bromide as a phase transfer catalyst is described.

Halogenation is an important synthetic strategy for preparation of halogenated aromatic compounds which are of great importance as intermediates in pharmaceutical, pesticide, agrochemical industries, *etc*. The classical direct halogenation (chlorination and bromination) of aromatic compounds suffers from waste of halogen if halogen is employed. In large scale operations this is an environmental as well as an economical problem. A possible solution is to recycle the byproduct, *i.e.* HCl or HBr. These problems can be overcome by use of haloacid in presence of an oxidising agent, the method is found to be very effective and avoids the waste of halogen and recycling of HCl or HBr and hence can be said as ecofriendly.

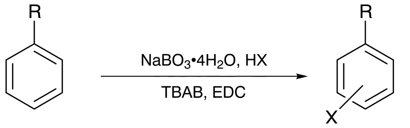
Halogenation of an aromatic ring by aqueous HCl or HBr using hydrogen peroxide as an oxidising agent has already been attempted.[1] However, the strong oxidising nature of H_2O_2 makes the method less selective, also H_2O_2 is hazardous and not easily handled, therefore this method is not convenient for large scale synthesis.

Sodium perborate is a very cheap, safe and easy to handle and therefore the ability of sodium perborate to release oxidative species in organic medium has made it a useful reagent in organic synthesis.[2,3] By considering all these properties of sodium perborate it has been successfully employed as a convenient substituent for H_2O_2 in various oxidation reactions. Also sodium perborate is widely used for selective functional group transformation,[4,6] however, as yet it has not been used for halogenation reactions.

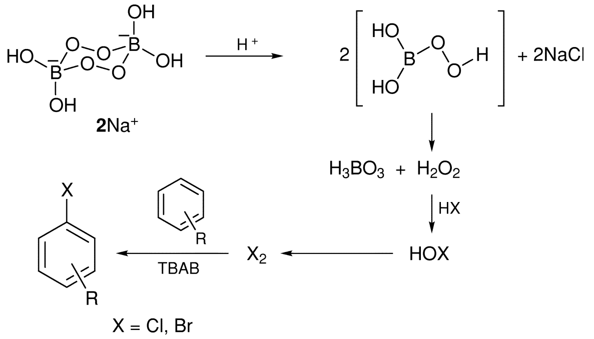
At present continuous research is directed to modified and improved procedures for higher efficiency and cleaner selectivity considering economic and environmental problems. In light of this, the properties of sodium perborate and the importance of halogenation reactions, we report here, an exceptionally simple yet efficient method for the halogenation of aromatic compounds by aqueous haloacids using sodium perborate as an oxidising agent in the presence of tetrabutylammonium bromide (TBAB) as a phase transfer catalyst (Scheme 1).

The results of the synthesis of various halogenated compounds are given in Table 1.

Activated benzene rings undergo halogenation smoothly to yield a mixture of both *ortho* and *para* substituted products, whereas deactivated rings do not undergo halogenation even after a prolonged reaction time.



Scheme 1



Scheme 2

Sodium perborate oxidises haloacid to hypohalous acid which is a slower halogenating agent compared to halogen, as HO^- is a poorer leaving group from HOX than X^- is from X_2. The reaction is speeded up in the presence of TBAB, as HOX is then converted into the more reactive X_2. TBAB acts as a phase transfer catalyst and as a Lewis acid in the halogenation of aromatic compounds. The probable mechanism is shown in Scheme 2. Halogen molecules are known to be activated by quaternary ammonium salts for electrophilic attack on the aromatic ring. This may well be achieved by the formation of adducts of general structure R_4NX_n ($n = 3$ or 5) in which the halogen molecules are partially polarized. This type of adduct is known to function as a mild halogenating agent.[7] Probably due to this, only activated aromatic rings undergo electrophilic substitution under the reaction condition used.

In conclusion, the present procedure is simple and convenient. In addition the reagent used, sodium perborate, is inexpensive, non-toxic, easy to handle and does not involve any effluent or byproduct problem.

Experimental

GC analysis were performed on a Chromosorb W AW DMCS, using a 10 ft × 1/8 in 20% SE–30 column.

Table 1 Halogenation of aromatic compounds using sodium perborate as oxidant

		Chlorination			Bromination		
R	Reaction time/h	*o*-	*p*-	Yield (%)	*o*-	*p*-	Yield (%)
Me	6	40	57	74	37	60	78
H	6	—	—	90[a]	—	—	88[a]
OMe	6	—	100	66	—	100	70
OH	2	22	78	80	20	80	77
COMe	24	—	—	0	—	—	0
CO_2H	24	—	—	0	—	—	0
NO_2	24	—	—	0	—	—	0

[a] Reaction proceeds up to the monohalogenated state, no dihaloganated product was observed by GC analysis.

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General Experimental Procedure.—To a well stirred mixture of sodium perborate (10 mmol) and tetrabutylammonium bromide (0.1 mmol) in 1,2-dichloroethane (15 ml), was added aqueous haloacid (HCl, HBr) (12 mmol) followed by addition of an aromatic compound (1 mmol).

The final reaction mixture was stirred at 65 °C. The progress of reaction was monitored by TLC. After completion of the reaction 20 ml of water was added and organic layer was separated which was then washed with water (2 × 10 ml). The organic solvent was then removed by rotary evaporation at reduced pressure. The product obtained was analysed by GC and by its physical properties.

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