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Pyridinium bromochromate: a new and efficient reagent for bromination of hydroxy aromatics

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Abstract—Pyridinium bromochromate (PBC) has been used as an efficient and selective nuclear brominating agent for bromination of various substituted hydroxy-acetophenones, aldehydes and phenols. © 2003 Published by Elsevier Science Ltd.

Molecular bromine in acetic acid or chloroform and KBr plus $KBrO_3$ in aqueous solution are good brominating agents for organic substrates, but molecular bromine is hazardous and its vapours are irritating. Moreover, aqueous KBr–$KBrO_3$ cannot be used for many substrates since they are insoluble in water. Both brominating agents cause nuclear as well as side-chain bromination. The present paper reports the use of pyridinium bromochromate (PBC) in acetic acid as a selective brominating agent for hydroxy aromatic compounds.

The hydroxy aromatics and PBC were dissolved in the minimum amount of glacial acetic acid and the reaction mixtures were heated on a water-bath with constant stirring. Completion of the reaction was checked by TLC and the colour of the reaction mixture (green) acts as an indicator monitoring the progress of the reaction. The time required for the reaction was 20–45 min; the contents were then poured into water. The brominated products so obtained were recrystallized from aqueous ethanol. The structures of the products were confirmed by IR, ^{1}H NMR, halogen analysis and by comparing their melting points with those of samples prepared by known literature methods (Table 1).[1–4]

Bromination of hydroxyacetophenone by PBC has the following advantages: the procedure is simple; the isolation of the product is easy; the PBC reagent is easy to handle, can be weighed and has no hazardous effect, cf. bromine; only nuclear bromination occurs, no side-chain bromination being observed for hydroxy ketones.

Preparation of pyridinium bromochromate: this was synthesised[6] by taking 20 g (0.2 mol) of chromium trioxide in water (25 ml), cooled to 0°C. To this solution, 47% HBr (38 ml, 0.21 mol) was added slowly with constant stirring. The contents were cooled to 0°C and then pyridine (16.3 ml, 0.2 mol) was added over 15–20 min, to give a brown solid. The reaction mixture was chilled for 4–5 h. The dark brown crystals were then filtered and dried. The product was recrystallized from aqueous acetic acid (40:60 v/v) and its purity was checked by TLC and confirmed by melting point and elemental analysis (108°C).

A typical procedure for bromination: A mixture of 4′-hydroxyacetophenone (1.36 g, 0.01 mol) and PBC (2.58 g, 0.01 mol) in glacial acetic acid (8–10 ml) was heated on a water bath for a few minutes. After the reaction was completed (TLC and when a green colour appeared in the reaction mixture) the contents were poured into ice-cold water. The solid thus obtained was filtered, washed with water and crystallised from aqueous ethanol.

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Table 1. Bromination of hydroxy aromatics by pyridinium bromochromate

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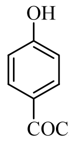
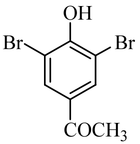
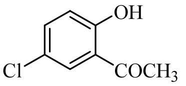
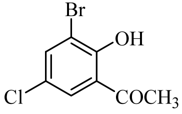
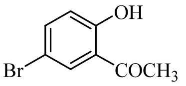
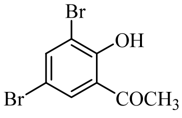
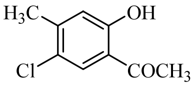
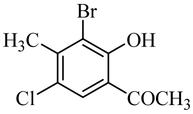
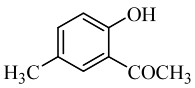
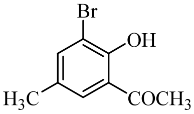
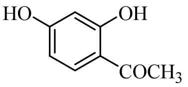
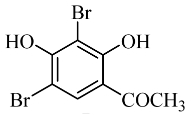
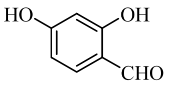
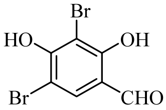
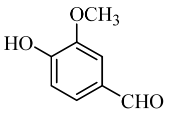
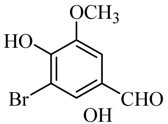
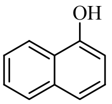
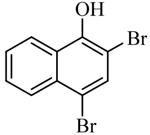
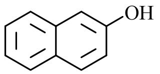
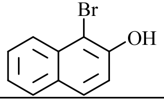
1			93[5]
2			95[5]
3			94[5]
4			91[5]
5			88[5]
6			89[5]
7			95[5]
8			96
9			92
10			85

[a] Refers to isolated yields

[b] All the products exhibited the expected analytical and spectral data.

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