

Bromination of *o*-Hydroxyacetophenones and *o*-Hydroxychalcones with Potassium Bromide-Potassium Bromate

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Bromination of *o*-hydroxyacetophenones (I) and 2'-hydroxychalcones (IV) with KBr-KBrO₃ in glacial acetic acid medium gave corresponding nuclear substituted 3-bromo-2-hydroxy-acetophenone (II) and 3'-bromo-2'-hydroxychalcone(V) derivatives respectively. However, bromination of 2'-hydroxy-5'-methylchalcone (IVc) resulted in 8-bromo-6-methylflavanone (VI). All the synthesised compounds have been characterised by elemental analysis and spectral data.

INTRODUCTION

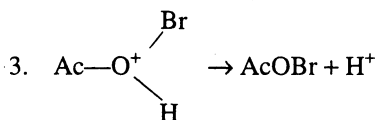
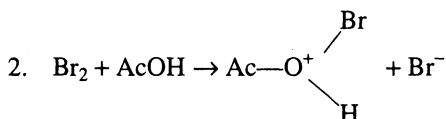
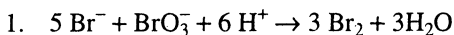
The bromination of aromatic compounds still holds its charm to the synthetic organic chemists as is evident from the work of McKillop and Bromley¹. Recently bromination of *o*-hydroxyacetophenones²⁻⁶ and 2'-hydroxychalcones^{7,8} with different brominating agents have given interesting results. The observations⁹⁻¹¹ that potassium bromate under acidic condition is a unique brominating agent for aromatic compounds alone or along with potassium bromide prompted us to study the bromination of some *o*-hydroxyacetophenones and their condensation products with aromatic aldehydes generally known as 2'-hydroxychalcone.

RESULTS AND DISCUSSION

In the present investigation firstly the reaction of substituted *o*-hydroxyacetophenones (I) was carried out with KBr-KBrO₃ mixture in acetic acid at room temperature. The resulting acetophenones were identified as 3-bromo-2-hydroxyacetophenones (II) on the basis of compounds reported in literature and IR spectra. In another attempt *o*-hydroxychalcones (IV) were prepared by condensing suitably substituted *o*-hydroxyacetophenones (I) with aromatic aldehydes (III) in presence of base. The resultant chalcone (IV) was brominated by KBr-KBrO₃ in presence of acetic acid at room temperature. These compounds were characterised as 3'-bromo-2'-hydroxychalcone (V) by its elemental analysis and IR spectra. These compounds showed carbonyl frequency at 1650 cm⁻¹ and two major aromatic frequencies in the regions 1580–1570 cm⁻¹ and 1460–1430 cm⁻¹. The —CH deformation frequencies characteristic of *trans*-ethylenes are found in the region 1350–1300 cm⁻¹ and 1000–950 cm⁻¹. Final confirmation of bromochalcones (V) was done on the basis of independent synthesis of these compounds by condensing appropriate bromoacetophenones (II) with suitably substituted aromatic aldehydes (III) and by m.m.p. co-TLC and superimposable IR spectra. However, bromination of 2'-hydroxy-5'-methyl chalcone (IVc) under identical

conditions resulted in 8-bromo-6-methylflavanone (VI) in place of 3'-bromo-2'-hydroxy-5'-methylchalcone. IR spectra of (VI) showed carbonyl absorption at 1700 cm^{-1} . The course of this reaction may involve bromination of chalcone followed by cyclisation in acidic medium.

The use of KBr-KBrO_3 avoids possible hazards of using elemental bromine. It is likely that bromination with this reagent in glacial acetic acid may take place through the following steps involving bromine cation in the solvent as the conjugate acid of acetyl hypobromide (2) or as the hypobromide itself (3).



EXPERIMENTAL

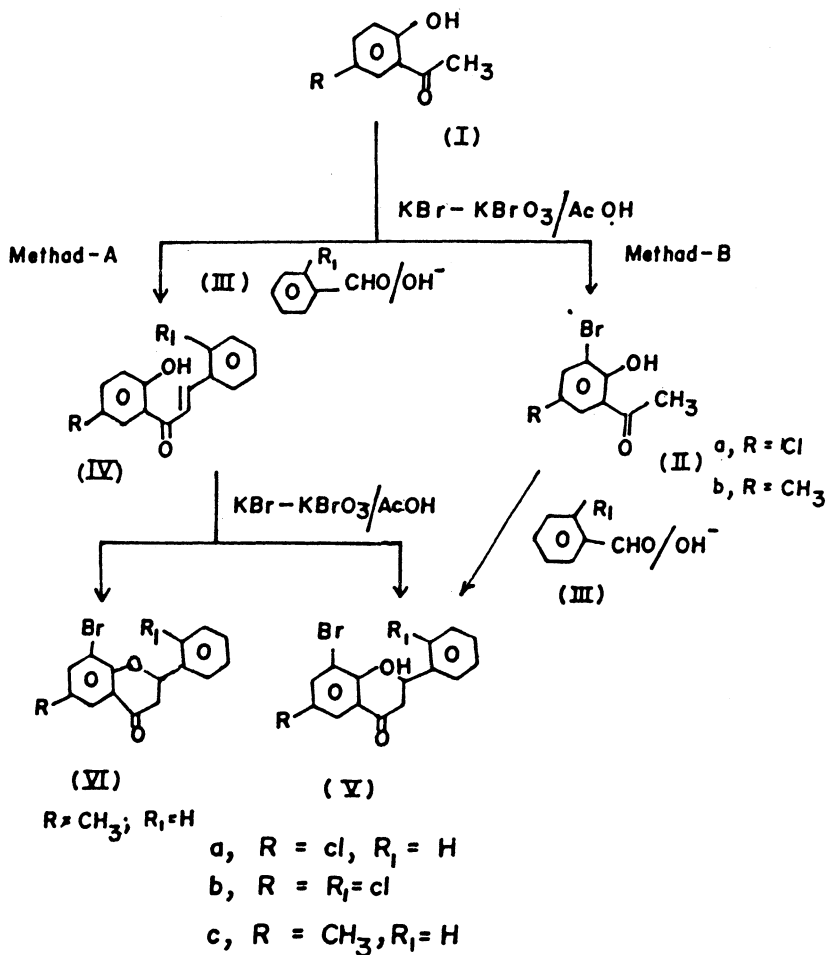
All melting points were taken in open capillary tubes and are uncorrected. IR spectra (KBr) were recorded on a PILAB FTS14 spectrophotometer ($\nu_{\text{max}}\text{ cm}^{-1}$). Purity of the products was checked by TLC on silica gel-G coated glass plates of 2 mm thickness using benzene-ethylacetate (9:1; v/v) and spots were visualized by exposure to iodine vapours in a closed chamber. Satisfactory elemental analysis was obtained for all compounds. *o*-Hydroxyacetophenones¹²⁻¹⁴ (I) and 2'-hydroxy-chalcones^{15, 16} (IV) were prepared by literature methods.

Bromination of *o*-hydroxyacetophenones (I)/2'-hydroxychalcones (IV)

Variously substituted *o*-hydroxyacetophenones (0.01 mole)/2'-hydroxychalcones (0.01 mole) were dissolved in glacial acetic acid (20 mL). To this solution a mixture of potassium bromate (0.55 g) and potassium bromide (2.0 g) in glacial acetic acid (30 mL) was added with constant stirring (30 min) and kept overnight at room temperature. The reaction mixture was poured into water (100 mL) and the separated solid filtered, washed with water ($3 \times 50\text{ mL}$), dried and recrystallised from petroleum-ether ($40-60^\circ\text{C}$) as colourless needles of (II) and rectified spirit gave yellow needles in the case of (V). Using the above procedure the following bromoacetophenones(II) and bromochalcones (V) were prepared.

Compound IIa	—	m.p. 92°C (lit. ¹⁷ m.p. 92°C); yield 56%; found C, 37.86; H, 2.26%; $\text{C}_8\text{H}_6\text{O}_2\text{BrCl}$ requires C, 38.47, H, 2.40%; IR, 1650 cm^{-1} $\nu(\text{C}=\text{O})$.
Compound IIb	—	m.p. 90°C (lit. ¹⁸ m.p. 89°C); yield 73%; found C, 46.66, H, 4.01%; $\text{C}_9\text{H}_9\text{O}_2\text{Br}$ requires C, 47.16, H, 3.93%.

Compound Va	–	Method A, m.p. 135–136°C; yield 50%. Method B, m.p. 136°C; yield 74%; found C, 53.16; H, 2.83%; C ₁₅ H ₁₀ O ₂ BrCl requires C, 53.41; H, 2.96%.
Compound Vb	–	Method A, m.p. 138°C; yield 56%. Method B, m.p. 139°C; yield 50%; found C, 48.38; H, 2.41%.
Compound Vc	–	Method B, m.p. 110°C (lit. ¹⁹ m.p. 108°C); yield 69%; found C, 59.58, H, 4.06%, C ₁₆ H ₁₃ O ₂ Br requires C, 60.56, H, 4.10%
Compound VI	–	8-Bromo-6-methyl flavanone. Method A, m.p. 106°C (lit. ¹⁷ m.p. 104°C); yield 58%, IR 1700 cm ⁻¹ ν(C=O).



Scheme I

ACKNOWLEDGEMENT

The authors thank the Head, Department of Chemistry, College of Science, M.L. Sukhadia University, Udaipur for providing laboratory facilities.

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(Received: 20 February 1996; Accepted: 1 July 1996)

AJC-1119