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A *green* Hunsdiecker reaction: synthesis of β-bromostyrenes from the reaction of α,β-unsaturated aromatic carboxylic acids with KBr and H_2O_2 catalysed by $Na_2MoO_4{\cdot}2H_2O$ in aqueous medium

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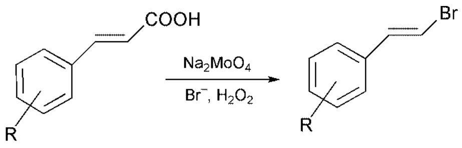
Reaction of α,β-unsaturated aromatic carboxylic acids with KBr and H_2O_2 in the presence of $Na_2MoO_4{\cdot}2H_2O$ in aqueous medium affords β-bromo alkenes in high yield.

The classical Hunsdiecker reaction and its later modifications are efficient for the synthesis of organic halides.[1] However, these reactions have major limitations, such as toxicity and hazard involving use of elemental bromine, salts of Hg(II), Tl(I), Pb(IV), Ag(I). Apart from this, very poor yields of the products are obtained in the cases of α,β-unsaturated aromatic carboxylic acids. Recently, some of these difficulties have been overcome by the use of lithium acetate as the catalyst and *N*-bromosuccinimide as the bromine source, the reaction medium being aqueous acetonitrile.[2] However, low yields were obtained in the cases of α,β-unsaturated aromatic carboxylic acids bearing electron-withdrawing groups in the aromatic ring.

Transition metal peroxo compounds have been shown to be efficient oxidising agents for various organic substrates.[3–6] Some marine organisms use a vanadium dependant enzyme, bromoperoxidase, for the bromination of organic compounds using inorganic bromides and hydrogen peroxide.[6] We have been investigating bromination of organic compounds using vanadium(V) or molybdenum(VI), potassium bromide, and hydrogen peroxide in aqueous medium.[7–9] It was observed that the transition metal peroxo complexes can oxidise inorganic bromide and produce Br_3^- species which is in equilibrium with HOBr and Br_2.

We thought that this biomimetic system could be utilised as an alternative route to the Hunsdiecker reaction. Herein we report the initial results of our studies on the reaction of α,β-unsaturated aromatic carboxylic acids with KBr and H_2O_2 in aqueous medium in the presence of $Na_2MoO_4{\cdot}2H_2O$.

When a suspension of α,β-unsaturated aromatic carboxylic acid (0.02 mol) is stirred with KBr (0.04 mol) and $Na_2MoO_4{\cdot}2H_2O$ (0.001 mol) in water (5 cm^3) and H_2O_2 (15 cm^3, 0.13 mol) is added drop-wise at room temperature (30 °C), a rapid reaction takes place and the temperature rises to 80 °C within 20 min. The reaction mixture was stirred for further 20 min and the product as well as the unreacted acid was extracted with diethyl ether. The corresponding β-bromostyrene was separated from the starting material by column chromatography in good yield (Scheme 1). The yield of the styrene is very good in the cases of α,β-unsaturated aromatic carboxylic acid bearing a substitutent in the 4-position. For example, 3-(4-methoxyphenyl)prop-2-enoic acid and 3-(4-chlorophenyl)prop-2-enoic acid yield the corresponding β-bromo alkenes in 85 and 65% yield respectively. It may be noted that for 3-(4-chlorophenyl)prop-2-enoic acid a larger amount of Na_2MoO_4 (acid–Mo, 10:1) is required for better yield. The unsubstituted acid also affords β-bromostyrene in good yield (65%). In the case of an acid bearing substituents in 2-positions, for example, 3-(2-chlorophenyl)prop-2-enoic acid and 3-(2-methylphenyl)-prop-2-enoic acid, the yield of the corresponding β-bromostyrene is very poor (5 and 15%, respectively). The evolution of CO_2 was detected by passing the outcoming gas through limewater. It may be noted that this is the first report of isolation of Hunsdiecker products in water. All the earlier reports deal with the reactions in non-aqueous medium.



R = H or 4-OMe or 4-Cl or 2-Me or 2-Cl

Scheme 1

The solution of Na_2MoO_4 (0.001 mol) and KBr in H_2O (5 cm^3) is basic in nature (pH 10). Upon addition of solid acid, the pH of the slurry changes to 4.5. When H_2O_2 (15 cm^3) is added to the reaction mixture, the measured pH is 3.9. The pH of the reaction changes to 9 upon completion of the reaction. It has been shown by Rothenberg and Clark that a proton source is required for oxyhalogenation.[10] Thus in these reactions the proton source is the acid itself.

It has been shown earlier that, MoO_4^{2-} forms a number of peroxo species in solution in the presence of H_2O_2. The ^{95}Mo NMR spectra of a solution of Na_2MoO_4 (0.001 M) in H_2O_2 (15 cm^3) shows a major signal at −336 ppm and a relatively low intensity signal at −509 ppm. These are due to the formation of $[MoO(O_2)_3]^{2-}$ and $[Mo(O_2)_4]^{2-}$ species, respectively.[11] Upon addition of Br^- both the signals at −509 and −336 ppm disappear and two signals at −222 and −37 ppm appear. The signal at −222 ppm can be assigned to $[MoO(O_2)_2]^{2-}$.[11] The signal at −37 ppm may be assigned to a molybdate species coordinated to bromide. The slight shift in the observed ^{95}Mo NMR spectra from those of reported ones[11] may be due to the effect of pH as well as extent of hydration.

A blank reaction, which is a similar reaction without the addition of Na_2MoO_4, did not afford the brominated products. Thus, it is clear that bromide is oxidised by the peroxomolybdate species formed in solution.

The electronic spectrum of a solution (10^{-3} M) of Na_2MoO_4 in H_2O_2 (2×10^{-2} M) shows bands at 445 (ε = 162) and at 293 nm (ε = 1620 mol^{-1} dm^3 cm^{-1}). These are due to the tetraperoxo and triperoxomolybdate species.[11] When KBr is added to this solution an absorbance increase is observed in the region 700 to 290 nm. However, no new band appears. The molar extinction coefficient of the 445 nm band increases to 320 and the band at 293 nm shifts to 298 nm with increase in the molar extinction coefficient (ε = 1833). It may be noted that the oxidised bromide species, Br_2, Br_3^- and OBr^- absorb in the region, 450 to 300 nm. Meister and Butler[12] and our earlier work on the oxidation of Br^- by H_2O_2 in the presence of Mo(VI)[9] have shown that Mo(VI) first forms peroxomolybdate which then oxidises Br^- to form an equilibrium mixture of Br_2, Br_3^- and OBr^-. Thus it clear form the earlier work as well as from the present evidence that the peroxomolybdates generated

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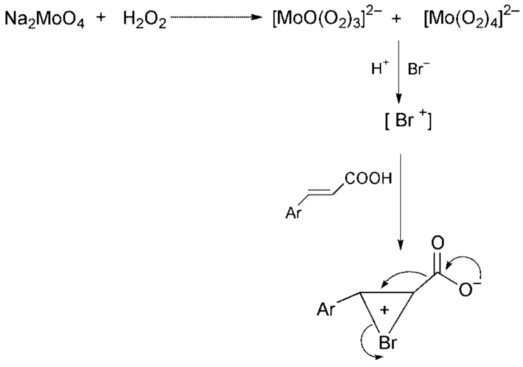

Scheme 2

from the reaction of H_2O_2 and MoO_4^{2-} react with Br^- to produce the equivalent of the Br^+ species, which then react with the unsaturated acid to give bromo alkene.

In order to identify the brominating species, reactions of Br_2 in aqueous KOH ($HOBr–OBr^-$) (pH = 10) as well as Br_2 in aqueous KBr (Br_3^-) with the acid in aqueous medium were carried out. But in both the cases we could only isolate the starting material. Thus, it is clear that the Mo center plays an important role, and probably the coordination of the acid is required for the conversion as observed in the case of vanadium bromoperoxidase.[13]

From the above spectral evidence, it may be inferred that, the reaction proceeds through an ionic mechanism (Scheme 2). It may be noted that a similar mechanism has been suggested by Roy *et al.* earlier.[2] The reason behind the low yield of the products in the cases of *ortho* substituted aromatic acids may be due to steric crowding of the intermediate bromonium species. The reactions described here show that the Hunsdiecker reaction can be brought about in aqueous medium, contrary to earlier reports, and also this is the greenest route to Hunsdiecker products.

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