Conversion of *o*-Hydroxyaldehydes and Ketones into *o*-Hydroxyanilides by Monochloramine

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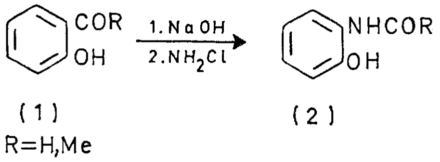
Summary Rearrangement of the sodium salts of salicylaldehyde, 2-hydroxyacetophenone, and *o*-vanillin by monochloramine yielded 2-formamidophenol (88%), 2-acetamidophenol (93%), and 2-formamido-6-methoxyphenol (75%), respectively.

WE report a novel reaction of *o*-hydroxy-aldehydes and ketones (**1**) with monochloramine. The simple, one-step procedure affords *o*-hydroxyanilides (**2**) in good yields.

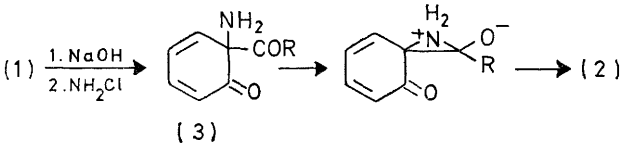
The general procedure entails addition of a solution of the sodium salt of the phenol (0·05 mol, 0 °C) to a cold, aqueous solution of monochloramine[1] (0·05—0·075 mol), followed by stirring for 4 h at 0°. Thus, salicylaldehyde gave 2-formamidophenol[2] (85—90%), 2-hydroxyacetophenone gave 2-acetamidophenol[2,3] (90—95%) and *o*-vanillin gave 2-formamido-6-methoxyphenol (65—85%), m.p. 123—124°.

4-Hydroxybenzaldehyde and 4-hydroxyacetophenone provided the corresponding amides in about 10% yield, and 3-hydroxyacetophenone did not react.



Although the method appears to work best with the *o*-substituted compounds, there would be reasonable scope since such substrates are available in variety from the Reimer–Tiemann reaction,[4] lignins,[5] essential oils,[6] and certain pigments[7] (flavones and anthraquinones). A distinct advantage of this technique is that the Beckmann[8] and Schmidt[9] rearrangements do not usually proceed well with aromatic aldehydes.

The reaction pathway conceivably involves nucleophilic displacement on monochloramine by the cyclohexadienone (phenoxide) anion to produce the aminoketone (**3**) analogous to the mechanistic postulate invoked for conversion of 2,6-disubstituted phenoxides into dihydroazepinones by exposure to monochloramine.[10] Our overall transformation bears similarity to the Beckmann, Schmidt, Theilacker, and Pearson rearrangements.[11]



I.r. and n.m.r. spectra were used for identification, in addition to microanalyses for the new compounds.

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