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

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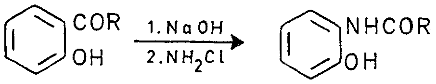
Summary Rearrangement of the sodium salts of salicylaldehyde, 2-hydroxyacetophenone, and *o*-vanillin by monochloramine yielded 2-formamidophenol (88%), 2-acetamidophenol (93%), and 2-formamido-6-methoxyphenol (75%), respectively.

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.

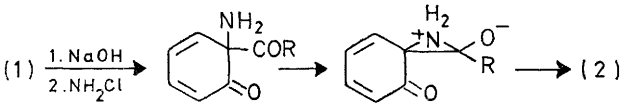


(1) (2)

R=H,Me

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]



(3)

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

We wish to thank the Center for Great Lakes Studies for financial support, and Messrs. B. L. Adams, R. E. White, and T. A. Wnuk for helpful discussions.

(*Received*, 9*th July* 1973; *Com.* 981.)

[1] P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, 1970, **70**, 639.

[2] E. Bamberger, *Chem. Ber.*, 1903, **36**, 2042.

[3] A. Ladenburg, *Chem. Ber.*, 1876, **9**, 1524.

[4] H. Wynberg, *Chem. Rev.*, 1960, **60**, 169.

[5] K. V. Sarkanen and C. H. Ludwig, 'Lignins,' Wiley-Interscience, 1971.

[6] E. Guenther, 'The Essential Oils', Van Nostrand, vol. II, 1952.

[7] K. W. Bentley, 'The Natural Pigments', Interscience, 1960.

[8] L. G. Donaruma and W. Z. Heldt, 'Organic Reactions, Wiley, vol. 11, 1960, p. 42.

[9] P. A. S. Smith in 'Molecular Rearrangements', ed. P. de Mayo, Interscience, vol. I, 1963, p. 518.

[10] L. A. Paquette, *J. Amer. Chem. Soc.*, 1963, **85**, 3288.

[11] C. A. Buehler and D. E. Pearson, 'Survey of Organic Syntheses', Wiley–Interscience, 1970, p. 494.