A Novel Oxidant - Clorine Dioxide for Some Terpenic Primary and Secondary Alcohols and Aldehydes

Alexander V. Kutchin, Larisa L. Frolova, Irina A. Dvornikova, Irina V. Dreval
Institute of Chemistry of the Komi Science Center, Uralian Division of RAS, 48 Pervomaiskaya St., Syktyvkar, 167610, fax (8212) 436677, E-mail: kav@chemi.komi.ru

Alcohols and aldehydes oxidation to corresponding carbonyl and carboxyl compounds is normally performed using Cr, Mn, Ag compounds. We propose a new method - oxidation with ClO₂, which has not been previously used in organic synthesis. ClO₂, a highly reactive oxidizing agent, is widely used in wood-pulp and paper industry for cellulose bleaching (degradation of residue lignin) [1, 2].

Terpenic alcohols and aldehydes - myrtenol (1), myrtenal (2), trans-verbenol (3), borneol (4), menthol, and benzhydrol (5), were chosen as substrates.

A number of parameters were studied affecting the transformation of the initial compounds and yields of resultant substances (solvent, temperature and time of reaction, method of oxidant supply).

In reaction (1), the solvent strongly affects the aldehyde: acid ratio: mixtures (2) (30-40%) and (6) (12-14%) are formed in CCl₄ medium; oxidation in benzene or acetone lead to myrtenic acid formation as the only product (50-55%); when the reaction was performed in ethanol, (6) was partly esterified. Oxidation of (3), (4), and (5) gave the corresponding ketones: verbenone (7), camphor (8) and benzophenone (9) with 25-80% yields. It was found out that menthol is not oxidized to menthone by chlorine dioxide under similar conditions.