DOI: 10.1002/cssc.200800193

Sustainable Synthesis of Aldehydes, Ketones or Acids from Neat Alcohols Using Nitrogen Dioxide Gas, and Related Reactions

M. Reza Naimi-Jamal,*[a] Hamideh Hamzeali,[b] Javad Mokhtari,[a] Jürgen Boy,[c] and Gerd Kaupp*[d]

Benzylic alcohols are quantitatively oxidized by gaseous nitrogen dioxide to give pure aromatic aldehydes. The reaction gas mixtures are transformed to nitric acid, which renders the processes free of waste. The exothermic gas–liquid or gas–solid reactions profit from the solubility of nitrogen dioxide in the neat benzylic alcohols. The acid formed impedes further oxidation of the benzaldehydes. The neat isolated benzaldehydes and nitrogen dioxide quantitatively give the benzoic acids. Solid long-chain primary alcohols are directly and quantitatively oxidized with nitrogen dioxide gas to give the fatty acids in the solid state. The oxidations with ubiquitous nitrogen dioxide are extended to solid heterocyclic thioamides, which gives disulfides, and to diphenylamine, which gives tetraphenylhydrazine. These sustainable (green) specific oxidation procedures produce no dangerous residues from the oxidizing agent or from auxiliaries.

Introduction

The oxidation of benzylic alcohols to benzaldehydes seems to be an important task in green chemistry. More than 40 different techniques using poisonous solvents, expensive catalysts, or solid supports and microwave techniques have been reported recently. Residues from the auxiliaries and non-quantitative conversion of reactants to the desired product create dangerous waste. Waste-free production techniques using cheap reagents are an important task in sustainable synthesis. NO_2/N_2O_4 is a little-used, ubiquitous though poisonous gaseous oxidation reagent.[1,2] It was first used in 1897 for the solvent-free oxidation of a benzylic alcohol, giving the aldehyde in 74–76% yield.[3] N_2O_4 was later used in $CHCl_3$ or CCl_4 solution for the oxidation of benzyl alcohols to give 81–98% of benzaldehydes after extended workup[4,5] but without easy and safe recycling of the reaction gases obtained, or in CH_2Cl_2 solution with activated charcoal to give the aldehydes in 70–98% yield after chromatographic workup.[6] Similar oxidations in liquid or supercritical CO_2 provided the aldehydes in 100% yield, but the separation of the reaction gases from the CO_2 remained unsolved.[7] A solvent-free process at ambient pressure with gaseous NO_2 to give 100% yield of the product and with easy separation of the reaction gases for further use is certainly superior.[1,2] We report herein the waste-free specific oxidations of benzylic alcohols, solid fatty alcohols, aromatic aldehydes, heterocyclic thioamides, and diphenylamine that give 100% yield of the product in most cases.

Results and Discussion

Benzylic Primary Alcohols

As liquid benzyl alcohol (**1a**) and its methyl- or methoxy-substituted derivatives **1b**–**e** exhibit comparatively low melting points and as NO_2 gas condenses easily, it is more practical to pursue their reactions in the solvent-free liquid state at ambient or slightly elevated temperatures. However, the oxidations of **1i**–**k** were also performed as gas–solid reactions at lower temperatures with very slow addition (6 h) of the NO_2 gas (Scheme 1).[2] Both methods are possible, as 1) NO_2 gas dissolves readily in compounds **1** often with melting of the crystals and 2) it is highly reactive. Apart from the aldehydes **2**, nitrous acid is initially formed. The latter undergoes its well-known decomposition to produce nitric acid, NO, and H_2O. As NO_2 reacts with H_2O to give additional $HONO_2$ and NO, the stoichiometry of the reaction can be described as shown in Scheme 1. It is insofar incomplete, because for practical reasons (avoid NO gas blanket) excess NO_2 was used (Experimental Section) and also because NO and NO_2 equilibrate with N_2O_3 (full IR data in the Supporting Information). Follow-up oxidations of the benzaldehydes to the corresponding benzoic acids are sufficiently impeded. As their IR bands in the pres-

[a] *Dr. M. R. Naimi-Jamal, J. Mokhtari*
Department of Chemistry, Iran University of Science and Technology
Tehran 16846 (Iran)
Fax: (+98) 2122292456
E-mail: naimi@iust.ac.ir

[b] *H. Hamzeali*
Islamic Azad University of Saveh, Saveh (Iran)

[c] *Dr. J. Boy*
Bad Zwischenahn, Mühlenbruch 1a (Germany)

[d] *Prof. Dr. G. Kaupp*
FB Chemie, University of Oldenburg
Diekweg 15, Edewecht (Germany)
Fax: (+49) 4486920704
E-mail: gerd.kaupp@uni-oldenburg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.200800193.

