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An efficient 1,2-deoxygenation method for the biomass-derived polyols glycerol and erythritol. Mechanistic studies of a formic acid-mediated deoxygenation†

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An efficient 1,2-deoxygenation method, involving an unexpected mechanism, was found for simple diols and for biomass-derived polyols (glycerol and erythritol) that results in the conversion of the 1,2-dihydroxy group to a carbon–carbon double bond.

Biomass is an abundant and readily available feedstock that has great potential as a renewable source of chemical intermediates.1 Whereas the preparation of useful chemicals from petroleum has historically been accomplished by adding heteroatom functionality to unfunctionalized starting materials, the conversion of biomass commonly requires the removal of oxygen atoms from the natural precursors. In this context, the deoxygenation of polyhydroxy compounds, especially biomass-derived carbohydrates, is an important target.

Glycerol (1) is the main byproduct in the triglyceride transesterification process for biodiesel manufacture. The recent market expansion of biofuels has made glycerol attractive as a starting material for the synthesis of more valuable chemicals.2 We describe in this paper an improved and efficient method for the formic acid-mediated conversion of glycerol into allyl alcohol (3) (Fig. 1). Allyl alcohol is a large-scale industrial chemical, presently produced from propene, which is used as a starting material in the manufacture of various polymers and other allyl compounds, and has also a great potential as a precursor of 3-hydroxypropionic acid,3 an important building block for the development of bio-refinery processes. Ours is a solvent-free procedure that employs formic acid while directing a stream of nitrogen over K2CO3. Besides protecting the product from atmospheric oxidation, the nitrogen bubbling facilitates distillation of the alcohol.

With respect to the mechanism of this reaction, our first hypothesis was that it involved initial acid-induced dehydration of glycerol to acrolein via a 1,2-hydrogen shift pathway, followed by reduction of the aldehyde carbonyl group consistent with the well-documented role of formic acid as a hydride donor.4 In order to test this hypothesis, we carried out isotopic labeling experiments using d5-glycerol (1-d5) and perdeuterated formic acid (2-d2) (Scheme 1). The incorporation of deuterium in the final product was monitored by 2H-NMR. First, d5-glycerol was treated with undeuterated formic acid and, surprisingly, no protons were incorporated from the supposed reducing agent formic acid into the product alcohol. Instead, the allyl alcohol product was completely deuterated at all carbon positions (3-d9).

Earlier studies5 reported substantial charring during the treatment of glycerol with formic acid. We have now found that simple expedient of protecting this reaction from air provides a much more tractable process. Specifically, treating glycerol with formic acid while directing a stream of nitrogen through the reaction mixture completely eliminates charring, which is mainly responsible for the formation of undesired products. The method thus substantially improves the yield and selectivity of the process. A description of our reaction conditions and full experimental details are presented in the supplementary information.†

By continuously removing the sensitive product alcohol (the most volatile component of the reaction mixture) by distillation, the high temperature can be maintained while allowing the reaction to proceed nearly to completion, resulting in a yield of 80% after purification by distillation over K2CO3. Besides protecting the product from atmospheric oxidation, the nitrogen bubbling facilitates distillation of the alcohol.

Fig. 1 Formic acid-mediated deoxygenation of the biomass-derived polyols glycerol and erythritol.

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reaction with non-labeled \(1\), no deuterium was incorporated in the final product \(3\), except for the exchange of deuterium into the hydroxyl group \(3\text{-d}1\) and the formyl proton of the minor allyl ester \(4\text{-d}1\). Thus, there is no hydride transfer from formic acid, ruling out the intervention of the expected acrolein intermediate.

We concluded from the above experiments that formic acid was somehow inducing a direct removal of two hydroxy groups (didehydroxylation reaction) from glycerol. To examine the generality of this process, we studied the reaction of several simple diols (Scheme 2) following the same procedure.

The reaction was found applicable in the case of 1,2-diols such as 1,2-octanediol \(5\) and 1,2-decanediol \(6\) which smoothly underwent this conversion to the corresponding alkenes in yields over 90%. Cyclic diols including cis-1,2-cyclopentanediol \(7\), cis-1,2-cyclohexanediol \(8\) and cis-1,2-cyclooctanediol \(9\) afforded the corresponding cyclic olefins in high yields. Trihydroxy compounds such as 1,2,3-hexanetriol \(10\) and 1,2,6-trihydroxyhexane \(11\) led as well to the corresponding alkenes 17 and 18.

Deoxygenation of diols to produce olefins is a useful synthetic transformation that typically requires initial conversion of the vicinal diol into an activated group, which is subsequently transformed into an olefin in a further step.10 The formic acid-mediated didehydroxylation provides a one-step procedure that directly affords the alkenes in high yield and purity.

We suggest that these reactions proceed through an orthoester-type intermediate, inspired by Eastwood’s procedure for the conversion of vicinal diols to olefins using triethyl orthoformate and acetic anhydride11 and by the thermal decomposition observed for 2-acetoxy-1,3-dioxolanes.12 A proposed mechanism for the formic acid-mediated didehydroxylation of glycerol (eqn (1)) is given in Scheme 3. We suggest that the reaction involves the transient formation of a cyclic carbocation intermediate \(c\), which is resonance-stabilized by the two oxygen atoms vicinal to the cationic center. The preparation and characterization of 1,3-dioxolan-2-ylium ions from \(\alpha\)-glycols has been previously described.13 The most plausible route from the 1,3-dioxolan-2-ylium to the observed product involves attack of the carbonyl oxygen of formic acid to provide a 2-acyloxy-1,3-dioxolane \(d\), Scheme 3, which then undergoes thermal carbon dioxide elimination and hydrogen transfer to give an olefin and formic acid.

The fact that cis-1,2-cyclopentanediol \(7\) reacted cleanly with formic acid at high temperature to yield cyclopentene \(14\), while trans-1,2-cyclopentanediol did not form the olefin, suggested that the formic acid-mediated deoxygenation is a highly stereospecific syn elimination, which is in accordance with the pathway proposed above. In order to confirm this supposition, we subjected two stereoisomeric internal acyclic 1,2-diols to the reaction. Thus, treatment of \((3R*,4R*)\)-decane-3,4-diol \(19\) and \((3S*,4R*)\)-decane-3,4-diol \(21\) with formic acid \(2\) proceeded readily, generating the trans \(20\) and cis \(22\) isomers of 3-decene respectively (Scheme 4). The diol substrates and the deoxygenation products have magnetically different protons that lead to specific and distinguishable...
patterns. Both reactions were stereospecific as observed by NMR analysis of the crude distillates, in which no signals (<1%) due to the alkene with the opposite stereochemistry were detected in the spectra.

In order to demonstrate the capability of thermal transformation of the cyclic orthoesters of type b (Scheme 3) to generate a double bond, the synthesis of a 2-acloyxy-1,3-dioxolane from a 2-alkyloxy-1,3-dioxolane was carried out. 1,2-Decanediol (6) was used as a model system for this study. The 2-ethoxy-1,3-dioxolane derivative 23 was prepared and subsequently converted\textsuperscript{12} to the 2-acloyxy-1,3-dioxolane 24 (Scheme 5). When a mixture of dioxolanes 23 and 24 was carefully heated, the 2-acetoxy-1,3-dioxolane 24 was transformed into the olefin 13 at 40–48 °C, while compound 23 was unaffected.

The above results suggest that the formic acid-mediated didehydroxylation might be extendable to carbohydrates, an economically and environmentally important target. Preliminary results with sugar polyols are very promising. Erythritol (25) is a four-carbon sugar alcohol that is accessible through yeast or fungal fermentation of glucose from corn starch (Fig. 1). The reaction of 25 with formic acid at 210–220 °C, following the procedure described above for glycerol (1), gave a distillate that contained 2,5-dihydropyran (27) along with water and formic acid. A 39% yield of the pure dihydropyran 27 was isolated after purification by fractional distillation (Scheme 6).

To investigate the course of this reaction, cis-1,4-anhydro-erythritol (26) was prepared by acid-catalyzed cyclo-dehydration of erythritol with p-toluenesulfonic acid\textsuperscript{14} in 88% yield. Formic acid-mediated didehydroxylation of the cyclic product 26 afforded the corresponding olefin 27 in 87% yield after purification by redistillation. The reaction of 3,4-dihydroxybutene (28) with formic acid was also investigated, since it is a reasonable potential intermediate in the conversion of erythritol to 2,5-dihydropyran. If deoxygenation of the vicinal primary and secondary hydroxy groups (through an orthoester type intermediate) occurred, the diol 28 could possibly provide the product 27 by acid-catalyzed cyclo-dehydration (Scheme 6, path b). However, as shown in Scheme 6, 28 did not yield 2,5-dihydropyran when submitted to our standard formic acid-mediated didehydroxylation conditions, pointing to path a as the most plausible reaction pathway.

2,5-Dihydropyran (27) is presently prepared by ring closing metathesis or by catalytic rearrangement of vinyl oxirane.

The transformation of erythritol (25) to 2,5-dihydropyran (27) is a good example of how this reaction could offer an efficient approach to the conversion of biomass to value-added chemicals.

In conclusion, we have uncovered an improved selective one-pot, one-reagent deoxygenation technique for converting vicinal diols to unsaturated systems in high yields, and provide evidence for an unexpected concerted mechanism for the critical bond-changing processes in this transformation. Our preliminary results with inexpensive biomass-derived polyols suggest that the reaction of polyhydroxy compounds with formic acid will be a valuable alternative for the manufacture of reduced oxygen content products.

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Notes and references