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Letter

Vitamin B_{12}-catalyzed conversion of some γ- and δ-bromoalkanols to polyhydroxy alkanols

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Abstract

Vitamin B_{12}-catalyzed allylic dimerization of some γ- and δ-bromoalkanols with activated Zn-dust in mixture ethanol/water (1:1) has been studied. Investigated bromoalkanols were prepared from corresponding tertiary Δ^4- and Δ^5-alkenols by means of benzeneselenyl bromide and subjected to chemical reduction with vitamin B_{12}. All investigated bromoalkanols, after dehydrobromination, underwent to oxidative allylic coupling and hydratation in the presence of protic solvents to give predominantly polyhydroxy alkanols.

Keywords: Allylic coupling; Bromoalkanols; Dehydrobromination; Hydratation; Polyhydroxy alkanols; Vitamin B_{12}

1. Introduction

Vitamin B_{12}, "pigment of life", is not only co-enzyme which mediate a series of unusual biochemical transformations in vitro [1], it may also serves to the synthetic chemist as catalyst for oxidations, hydrogenations, reductive eliminations, reductions of functional groups, rearrangements [2]. Of special interest in organic synthesis is B_{12}-catalyzed radical C–C bond formation [3].

Chemical (with active Zn-dust or $NaBH_4$) or electrochemical reduction of cyanocob(III)alamin (vitamin B_{12}) affords Co(I)alamin, catalitically active species in these reactions, which reacts with haloalkanes (RX) to form organocob(III)alamins (Scheme 1). Carbon centred radical generated after Co–C bond homolysis undergoes typical free radical reactions: reductive eliminations, intermolecular coupling, rearrangements, etc.

2. Experimental

A 100 cm^3 flask, equipped with a magnetic stirrer bar, under Ar, was charged with activated Zn-dust (2.1 g, 30 mmol) and ammonium chloride (1.16 g, 20 mmol). Then, 2 mol% of vitamin B_{12} (with respect to a substrate 100%, 0.19 g, 014 mmol) dissolved in 20 cm^3 of ethanol was added. Mixture has been stirred for 30 min until the reduction of Co(III) from vitamin B_{12} to Co(I) was completed, which can be seen by change of colour from red to dark green. Bromoalkanol (7 mmol), prepared previously in the reaction of correspoding tertiary alkenol with PhSeBr [4], was dissolved in 25 cm^3 EtOH/H_2O (1:1) and added to the reaction mixture. After the stirring during 20 h at room temperature, mixture was washed with ice brine and extracted with dichloromethane

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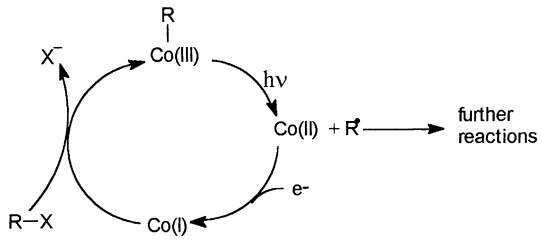


Scheme 1.

($3 \times 20\,cm^3$), dried over anh. Na_2SO_4 and evaporated in vacuo. Products were separated by flash chromatography (CH_2Cl_2 was eluent for phenylseleno ethers and MeOH for polyhydroxy alkanols) and fully characterised by spectroscopic methods.

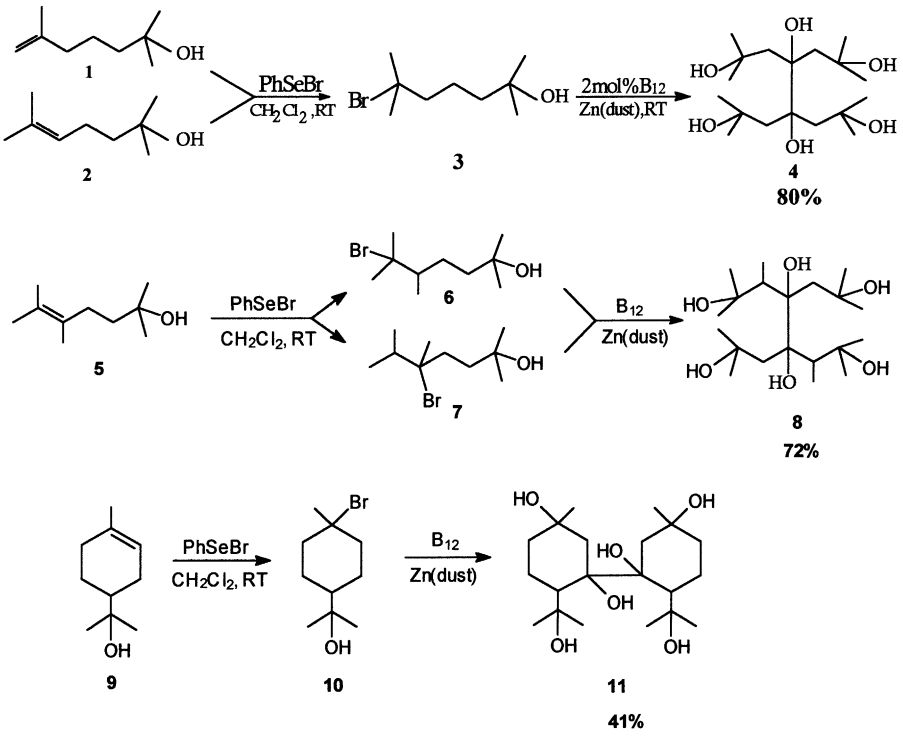
3. Results and discussion

Concerning our work on chemical reductions catalysed by vitamin B_{12} [5,6] we have now investigated the behaviour of γ- and δ-bromoalkanols.

In resent years, we have studied intramolecular cyclization of Δ^4- and Δ^5-alkenols by means of benzeneselenyl halides [4,7], PhSeX (X = Cl, Br). Intramolecular heterocyclization is the main reaction in the case of all investigated primary and secondary alkenols, while tertiary alkenols, under the same experimental conditions, are not converted into cyclic products at all by PhSeBr and in a small amount with PhSeCl. Although the additional products are expected, we have found that all investigated tertiary alkenols in the reaction with PhSeBr afforded γ- and δ-bromoalkanols in high yields (about 90%).

Both Δ^5-alkenol **1** and Δ^4-alkenol **2** gave the same δ-bromoalkanol **3** (Scheme 2). Δ^4-Alkenol **5** with tetrasubstituted double bond afforded the mixture of two possible regioisomers **6** and **7**, while α-terpineol **9** gave expected bromo product **10**.

These bromoalkanols have been further used as substrates and subjected in situ to chemical reduction in low acidic conditions (NH_4Cl) with 2 mol% of vitamin B_{12} and Zn-dust (Scheme 2) in mixture of EtOH/H_2O (1:1).



Scheme 2.

All investigated γ- and δ-bromoalkanols, after dehydrobromination, underwent to oxidative allylic coupling and hydratation in the presence of protic solvents (ethanol and water) to give predominantly polyhydroxy alkanols **4**, **8** and **11** (Scheme 2). The products were then isolated by extraction, separated by chromatography and analyzed by spectroscopic methods.[1] Reactions of bromoalkanols **3**, **6** and **7** proceeded in good yields (80 and 72%), while the cyclic bromoalkanol **10** gave the coupling product in lower yield (41%), due to the steric hindrance, and large amount of starting alkenol was recovered.

In all cases cyclic phenylseleno ethers were obtained as the minor products (10–20%) because the reactions were performed in situ and diphenyl diselenide was present in the rection mixture beside bromoalkanols. These cyclic products are identified on the basis of their NMR spectra [4].

Conversion of bromoalkanols to polyhydroxy alkanols by vitamin B_{12}-catalyzed elimination and oxidative allylic coupling in mixture of $EtOH/H_2O$ described herein illustrates the power and versatility of cyanocob(III)alamin as natural and nontoxic catalyst in organic synthesis.

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[1] Compounds were fully characterized by spectroscopic methods. Spectral data of 2,7-dimethyl-4,5-di(2-hydroxy-2-methylpropyl)-2,4,5,7-octantetraol (4) are given as an example: IR (film) 1150, 1500, 2850–2960, and 3620 cm^{-1}; ^1H NMR ($CDCl_3$) 1.48 (2H, m), 1.78 (12H, s, CH_3), 2.12 ppm (4H, m, CH_2), and 2.25 (6H, br s, OH) ppm; ^{13}C NMR (50.32 MHz, $CDCl_3$) 23.07 (CH_2), 34.07 (CH_3), 47.01 (CH_2), and 67.53 (COH) ppm.