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VACILLATING REACTIONS

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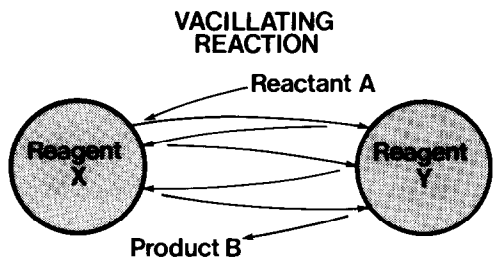
ABSTRACT: Addition of 1-dodecanol to a suspension of H_2CrO_4/SiO_2 plus $NaBD_4/Al_2O_3$ in ether at room temperature leads to the formation of 1-dodecanol-1,1-d_2.

We wish to describe a new synthetic technique which is based on the synergistic and multiple coupling of two supported reagents.[1] Our method takes advantage of the fact that reagents which are normally reactive toward one another in homogeneous solution are rendered compatible by immobilizing them onto separate insoluble supports.[2] Chemical systems which fall into this class are termed, "vacillating reactions". The following deuterium labeling of 1-dodecanol serves to illustrate the technique.



Current methods for incorporating deuterium into the C-1 position of primary alcohols normally involve oxidation--reduction reactions with carboxylic acids as intermediates (i.e., $RCH_2OH \longrightarrow RCO_2H \longrightarrow RCD_2OH$). Although this approach is satisfactory in many cases, it requires the use of strong oxidizing and reducing reagents and is not suitable for molecules bearing sensitive functional groups. Alternatively, partial oxidation to the corresponding aldehyde and reduction back to the alcohol can be accomplished using milder reagents; however, repeated redox cycles are needed to exchange both hydrogens with deuterium. Experimentally, this is not practical using conventional procedures. If the alcohol were subjected to

a mixed suspension of suitably supported oxidizing and reducing reagents, it should be able to undergo a continuous oxidation--reduction in one pot. The following results demonstrate the viability of this concept.

A 50-mL round-bottomed flask, equipped with a Teflon-coated magnetic stirring bar, was charged with 3.0 g of H_2CrO_4/SiO_2 (3.1 mmol of Cr), 1.7 g of $NaBD_4/Al_2O_3$ (14.4 mmol of D) and 8 mL of distilled ether, followed by addition of 0.22 mmol of 1-dodecanol.[3] The mixture was stirred at room temperature and the alcohol monitored periodically for deuterium content.[4] Figure 1 summarizes the results obtained. The overall formation of 1-dodecanol-1,1-d_2 clearly shows that the

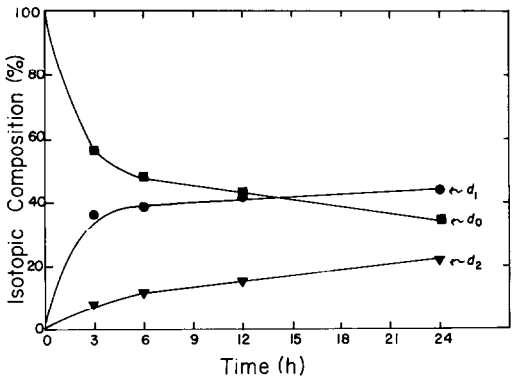


Figure 1

soluble alcohol undergoes continuous oxidation and reduction. While these data demonstrate that vacillating reactions are possible, the present systems suffers from relatively slow rates of conversion. Studies now in progress are aimed at optimizing this labeling procedure using fixed bed reactors and organic polymers as supports. Efforts are also being directed toward further applications of the vacillating reaction principle to other chemical transformations.

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4. Aliquots were reacted with bis(trimethylsilyl)acetamide in THF for 2 h at room temperature and the trimethylsilyl ether derivative analyzed for deuterium incorporation by GC-MS using a Finnegan 4000 instrument. Under the reaction conditions used, only a trace amount of aldehyde was detected in the product mixture.

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