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Asymmetric Protonation of Photodienols Enantioselective Synthesis of (R)-2-Methyl Alkanols

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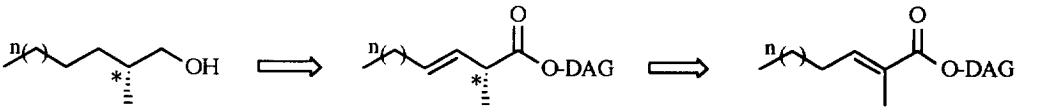
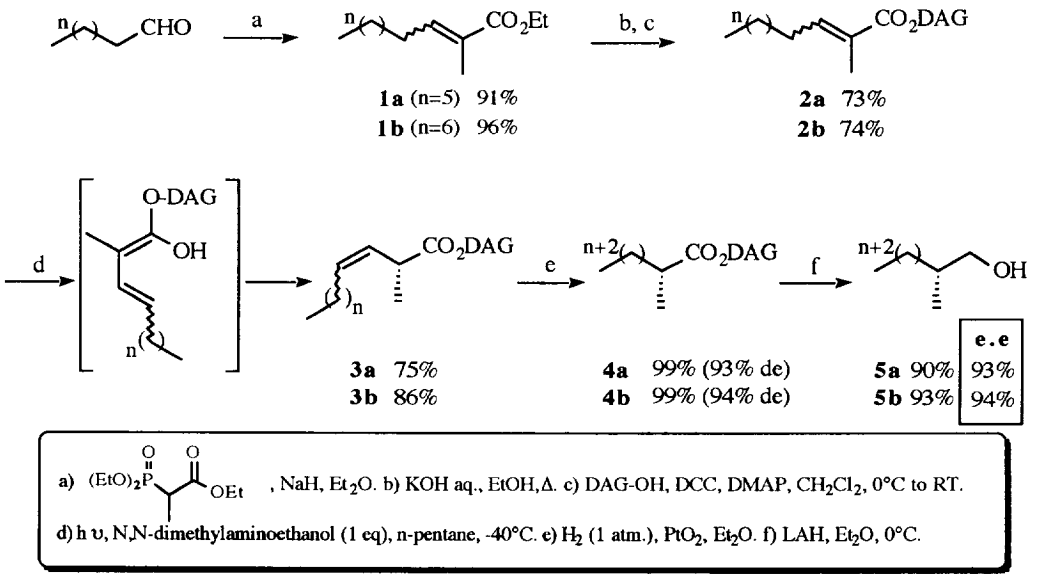
Abstract: *The enantioselective synthesis of (R)-2-methyl alkanols has been carried out by diastereoselective photodeconjugation and subsequent reduction of unsaturated esters bearing as chiral moiety, the diacetone D-glucose group.*

In the field of asymmetric photochemical processes, we recently reported the very highly diastereoselective photodeconjugation of α,β-unsaturated esters into optically active α-substituted β,γ-unsaturated isomers, using diacetone D-glucose (DAGOH) as the chiral inductor.[1] As an application of this reaction, we have chosen to perform the enantioselective synthesis of 2-methyl-1-decanol (n=5) and 2-methyl-1-undecanol (n=6) which exhibit important properties as aromas or perfumes[2] and whose asymmetric synthesis is still of importance.[3,4] Moreover, 2-methyl-1-decanol represents a useful precursor for the synthesis of 3,7-dimethylpentadecyl esters, constituents of the pheromone of pine sawflies.[5]



The starting materials **2a** (n=5) and **2b** (n=6) have been prepared in good yields by a Wittig-Horner reaction[6], followed by saponification[7] and esterification with DAG-OH using DCC activation[8]. Their irradiation in the presence of one equivalent of N,N-dimethylaminoethanol which is necessary to perform the selective protonation of one face of the prochiral photodienol intermediate, affords the β,γ-isomers **3a** and **3b** as an unseparable mixture of E and Z geometric forms. These have been directly hydrogenated in the presence of a catalytic amount of PtO_2, known to avoid racemization,[9] to the products **4a** and **4b**. The diastereoselectivities have been directly measured using ^{13}C-NMR spectra and compared to those of racemic compounds prepared by esterification of the racemic saturated acids with DAG-OH. They reached 93% and 94% de respectively for **4a** and **4b**. These esters have been reduced by the action of $LiAlH_4$ in diethyl ether giving the chiral 2-methylalkanols **5a** and **5b** in high optical purity[10] without loss of stereochemical integrity. The absolute configuration (R) is assigned by comparison of the sign of the specific rotation with previous data in the literature[3a,4a] and is in accord with the model already described for the protonation of the prochiral intermediate photodienol.[1] Furthermore, the procedure compares favourably with the direct hydrogenation of the conjugated

ester **2a** over PtO_2 which furnished **4a** in quantitative yields but with moderate diastereoselectivity (20% de), demonstrating the advantage of the two-step photochemical process.



In conclusion, the above sequence allows an entry to (R)-2-methylalkanols in good yields and very high optical purities and represent an alternative to recent methods which have used the selective reducing power of baker's yeast. Work is now in progress to apply the reaction to more elaborated targets.

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10. All new compounds have been characterized by ^{1}H-NMR, ^{13}C-NMR, IR, MS or by microanalysis.
5a: $[\alpha]_D$ = + 8.2 (3.0, $CHCl_3$), lit[4a] : (2R)-isomer $[\alpha]_D$ = + 8.7 (2.5, $CHCl_3$).
5b: $[\alpha]_D$ = + 9.6 (1.1, CH_2Cl_2), lit[3a] : (2S)-isomer $[\alpha]_D$ = -10.0 (4.2, CH_2Cl_2).

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