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New Method for the Asymmetric Reduction of Ketophosphonates

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New Method for the Asymmetric Reduction of Ketophosphonates

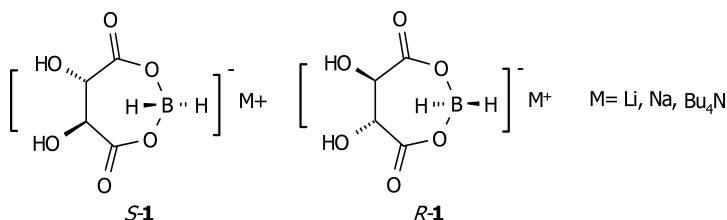
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Chiral reducing reactants were prepared from lithium, sodium, or tetrabutylammonium borohydrides and (S)- or (R)-tartaric acids.

Keywords Asymmetric reduction; chiral phosphonic acids; stereoselectivity

The chiral reducing reactants (S)-**1** or (R)-**1** were prepared from lithium, sodium, or tetrabutylammonium borohydrides and (S)- or (R)-tartaric acids.^{1,2}



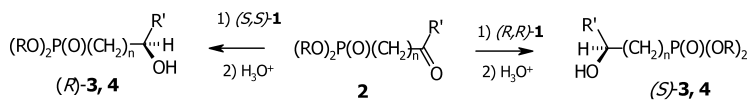
The reduction of α - or β -ketophosphonates with (S)- or (R)-**1** leads stereoselectively to the formation of (R)-, or (S)- α - or β -hydroxyphosphonates, correspondingly, in high yields and very good stereoselectivity.

The stereoselectivity of reaction depended on the absolute configurations of **1** and ketophosphonates. The reduction of di(1*R*, 2*S*, 5*R*)-menthyl ketophosphonates with the (R)-**1** proceeded with *matched* double asymmetric induction to give high enantiomeric excesses of hydroxyphosphonates (>96% *de*). The methodology was used for the preparation of enantiomerically pure phosphonate modified carnitine and other biologically active phosphonic acids in multigram scale.

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TABLE I Asymmetric Reduction of Ketophosphonates with Reagent (S)-1 or (R)-1 (R'O)₂P(O)(CH₂)_nCH(OH)R

R	R'	N	TA	Yield, %	ee (or de), %	Config.
CH ₂ Cl	MNT	1	<i>R, R</i>	93	96	<i>S</i>
CH ₂ Cl	ET	1	<i>R, R</i>	82	80	<i>S</i>
PH	ET	0	<i>R, R</i>	95	60	<i>S</i>
PH	MNT	0	<i>R, R</i>	95	92.5	<i>S</i>
PH	MNT	0	<i>S, S</i>	98	46	<i>R</i>
PH	ET	0	<i>S, S</i>	94	60	<i>R</i>
2-FC ₆ H ₄	MNT	0	<i>R, R</i>	97	82	<i>S</i>
2-AN	MNT	0	<i>R, R</i>	96	74	<i>S</i>
PYPERONYL	MNT	0	<i>R, R</i>	97	96	<i>S</i>

TA - Tartaric Acid, R=Et, Mnt (**3**), H (**4**)

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