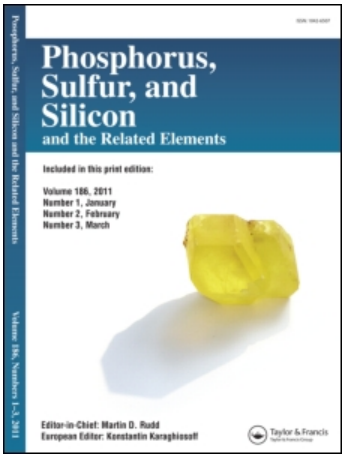

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New Method for the Asymmetric Reduction of Ketophosphonates

Vitaly V. Nesterov[a]; Oleg I. Kolodiazhnyi[a]
[a] Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

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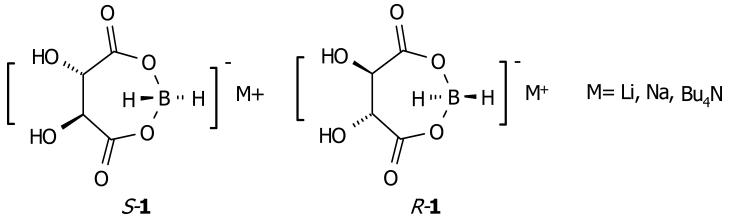
New Method for the Asymmetric Reduction of Ketophosphonates

Vitaly V. Nesterov and Oleg I. Kolodiazhnyi
Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

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

Keywords Asymmetric redution; 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]



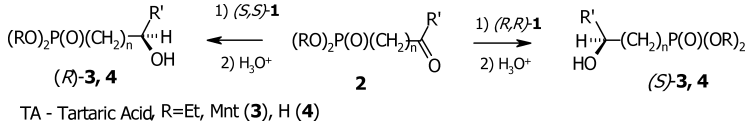
The reduction of α- or β-ketophosphonates with *(S)-* or *(R)*-**1** leads stereoselectively to the formation of *(R)-,* or *(S)*-α- or β-hydroxyphosphonates, correspondingly, in high yields and very good stereoselectivity.

The stereoselectivity of reaction depended on the absolute configurations of **1** and ketophosphonates. The reduction of di(*1R, 2S, 5R*)-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.

Address correspondence to Oleg I. Kolodiazhnyi, Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine. E-mail: oikol123@rambler.ru

TABLE I Asymmetric Reduction of Ketophophonates with Reagent *(S)*-1 or *(R)*-1 $(R'O)_2P(O)(CH_2)_nCH(OH)R$

R	R'	N	TA	Yield, %	*ee (or de)*, %	Config.
CH_2Cl	MNT	1	*R, R*	93	96	*S*
CH_2Cl	ET	1	*R, R*	82	80	*S*
PH	ET	0	*R, R*	95	60	*S*
PH	MNT	0	*R, R*	95	92.5	*S*
PH	MNT	0	*S, S*	98	46	*R*
PH	ET	0	*S, S*	94	60	*R*
2-FC_6H_4	MNT	0	*R, R*	97	82	*S*
2-AN	MNT	0	*R, R*	96	74	*S*
PYPERONYL	MNT	0	*R, R*	97	96	*S*



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[2] O. I. Kolodiazhnyi, *Tetrahedron: Asymmetry*, **16,** 3295 (2005).