Tetrahedron Vol 40, No 20, pp 4059 to 4065, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00

STEREOSELECTIVE ALDOL CONDENSATIONS VIA ALKENYLOXY DIALKOXYBORANES: SYNTHETIC APPLICATIONS USING THIOESTERS.

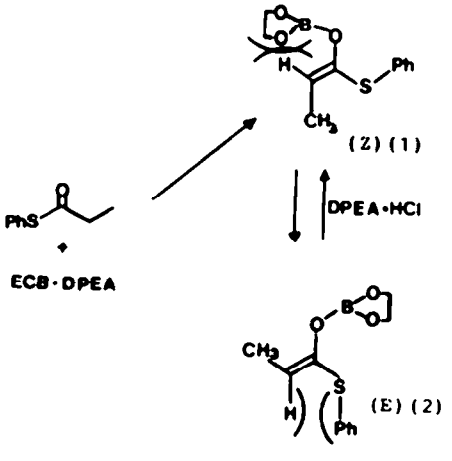
CESARE GENNARI*, ANNA BERNARDI, SILVIA CARDANI, AND CARLO SCOLASTICO

Istituto di Chimica Organica dell'Università e Centro CNR Sost. Org. Nat., via G.Venezian 21, 20133 MILANO, ITALY.

(*Received in UK 29 June 1984*)

Abstract- A detailed investigation of the enolization of phenyl thiopropionate with ethylenechloroboronate (ECB) and diisopropylethylamine (DPEA) and the subsequent aldol condensations of these enolates was conducted. Alkenyloxy dialkoxyboranes derived from thioesters were found to be stereoconvergent: both Z and E enolates give syn aldol condensation products. The thioester additions to chiral aldehydes were studied. Internal selectivity (syn) was usually very high, while the relative stereoselectivity ranged from poor to good, depending on the specific aldehyde used. The aldol products were transformed to known compounds for correlation.

Alkenyloxy dialkoxyboranes[1] have recently been shown to be useful reagents for regio- and stereoselective aldol condensations.[2-5] We report here the detailed steric course of the reaction of ethylenechloroboronate (ECB)-diisopropylethylamine (DPEA) complex with thioesters, and the synthetic applications of these enolates with achiral and chiral aldehydes. Enolization of phenyl thiopropionate with the ECB-DPEA complex proceeds very slowly from -78°C to 0°C, and is significant only from 0°C to RT. Slowly warming up the reaction mixture from -78°C to 0°C, or stirring directly at 0°C for 30 min, the enolization is incomplete and the Z/E[6] ratio observed by ^{1}H NMR analysis depends on the relative rates of formation of the Z enolate and of equilibration of the Z enolate to the more stable E one.[7] After stirring at RT for 30min with a slight excess of ECB-DPEA complex, no more starting material was observed and the ratio determined in this way by ^{1}H NMR is probably the fully equilibrated ratio at that temperature (Z-E 18:82). The kinetic enolization of thioesters is known to form predominantely Z enolates.[8] The reasons for this selectivity were discussed by Prof. Evans and coworkers in the cited papers[8].The only exception is the E enolate formation



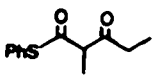
with phenyl thiopropionate and 9-BBNOTf, DPEA, 0°C,[9] which could well have arisen via the equilibration of the kinetic Z enolate.[10]

Entry	Enolization-conditions	(Z) (1)/ (E)(2)	Reaction with PhCHO d syn/anti(yield)	Reaction with n-$C_5H_{11}CHO$ d syn/anti(yield)
1	-78°/0°C,DPEA,CD_2Cl_2 a	70:30	95:5 (51%)	92:8 (41%)
2	0°C,DPEA, CD_2Cl_2 b	50:50	95:5 (63%)	92:8 (55%)
3	RT, DPEA, $CDCl_3$ c	18:82	95:5 (63%)	92:8 (53%)

a Slowly wormed up from -78° to 0°C, stirred at 0°C for 5 min. Incomplete enolization of the substrate was observed.
b Stirred for 30 min at 0°C. Incomplete enolization of the substrate was observed.
c Stirred for 30 min at RT.
d Reaction performed in methylene chloride from -78° to -20°C.

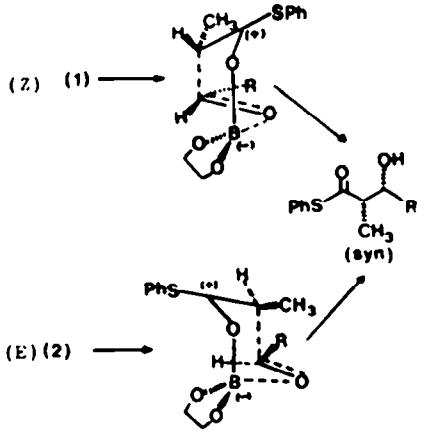
Alkenyloxy dialkoxyboranes are usually configurationally stable,[4] but they can equilibrate quite easily in the presence of the protonated amine.[5] A similar equilibration and an interesting discussion of the results have recently been reported for silyl ketene acetals.[7]

During the deprotonation step the only inconvenience is the formation of small amounts of the Claisen self-condensation product, but, as this reaction appears to be very slow even at RT, the wasted material is usually negligible (ca 5%).



The equilibrium mixture of the enolates was then frozen to -78°C, and aldehydes were added at that temperature. No aldehyde selfcondensation product was ever observed using various aldehydes (vide infra), and unreacted optically active aldehydes were reisolated after the reaction without loss of optical purity.

From all the examples reported, it is evident that these boron enolates are stereoconvergent.[11] Assuming a pericyclic transition state, it seems that the Z enolate prefers the boatlike process, while the E enolate prefers the chairlike. Both the enolates thus cooperate in producing syn[12] aldol condensation products.



This is in striking contrast to the case of alkenyloxy dialkylboranes,[8,9,10] which give a good correlation between the enolate geometry and the product aldol stereochemistry via a chairlike transition state. The different Lewis acidity of boron in these two classes of compounds could account for the difference in stereoselectivity. We are now undertaking computational studies in order to evaluate the different possibilities (acyclic, chairlike, boatlike processes) less superficially.

Additions to Chiral Aldehydes.

The issue of generating three stereocenters with a single reaction was then undertaken, taking advantage of the inherent syn selectivity of alkenyloxy dialkoxyboranes. Therefore the thioester additions to chiral aldehydes were studied. The results are briefly summarized as follows: a) acceptable yields, ranging from 50 to 60% were obtained. As the aldehyde is usually the more valuable material, the use of an excess (1.6 to 1.0) of the thioester enolate is recommended to complete the reaction with respect to the aldehyde component. b) The syn selectivity, using α-branched aldehydes, is increased. Anti compounds were barely detectable ($\leq$ 3%) with NMR (^{1}H, ^{13}C), VPC, HPLC analyses, and could not be isolated for inequivocal structural assignement. The only odd result reported is that in entry 8, where the major reaction product (55% of the mixture of diastereoisomers) is assigned as anti-A.C. This could be the result of strong chelation-control using a β-alkoxy aldehyde and perhaps another mechanism, different from the usual pericyclic one may be involved.[13] In this case we were not able to unambiguously correlate the minor isomers to known compounds as the ^{1}H NMR data of the remaining three diastereoisomers are very similar one to another and have been reported in an incomplete form.[14]

c) The relative stereoselectivity (Cram, cyclic Cram, Felkin models)[15] ranged from poor to good, depending on the specific aldehyde used.

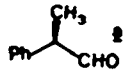
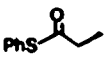
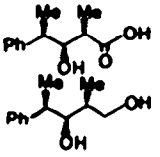
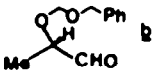
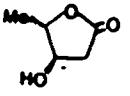
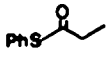
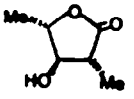
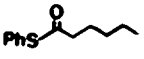
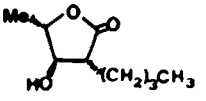
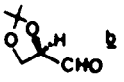
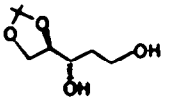
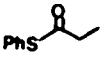
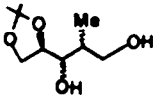
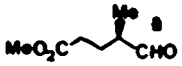
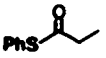
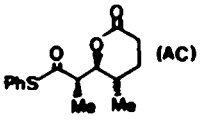
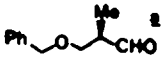
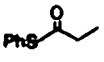
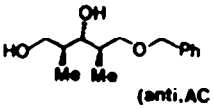
Examples permitting a quick attribution of the relative stereochemistry were chosen so that a comparison with the known, isolated and characterized, four possible stereoisomers could be made.[9,14,16-25] The ratios were determined by ^{1}H, ^{13}C NMR, VPC, and HPLC and are indicated using the following symbols: C=Cram, A.C.=antiCram, F=Felkin, C.C.=cyclicCram, S=syn, A=anti. The adducts were then transformed, by simple reactions to the suitable compounds for correlation.[9,14,16-25] Details of the transformations are reported in the experimental section.

We have therefore shown that alkenyloxy dialkoxyboranes are useful reagents for acyclic stereoselection and for the synthesis of natural products. We are currently working with chiral, non-racemic 1,2- diols as boron ligands and we hope that these new reagents will enhance the relative-stereochemistry ratios.

EXPERIMENTAL

General Procedure for the Aldol Condensations.

To a stirred solution of ECB (see ref.2) (1.1 mmol) and DPEA (1.15 mmol) in methylene chloride (2.5ml), at 0°C, under nitrogen, the thioester was added dropwise (1.0 mmol). The mixture was stirred at +5°C for 30 min, then cooled to -78°C and the aldehyde (0.625-1.0 mmol) was added at -78°C. The reaction was stirred at that temperature for 30 min, slowly warmed up to 0°C, and then quenched by adding pH 7-phosphate buffer. The product was extracted into methylene chloride, the extracts were dried (Na_2SO_4) and evaporated. The crude product was analyzed by ^{1}H, ^{13}C NMR spectroscopy and by HPLC for determining ratios. The compounds were then isolated

Entry	Aldehyde	Thioester	Internal Relative Stereochemistry	Correlated to (major)
1	 a		S/A ≥ 20:1 C/A.C.≥ 9:1	
2	 b		- F/C.C. 1.1:1	
3	" b		S/A ≥ 30:1 F/C.C. 2:1	
4	" b		S/A ≥ 30:1 F/C.C. 2.5:1	
5	 b		- F/C.C. ≥ 4:1	
6	" b		S/A ≥ 30:1 F/C.C. ≥ 7:1	
7	 a		S/A ≥ 30:1 C/A.C. 1:1	 (AC)
8	 a		- -	 (anti.AC)

a racemate; b optically active.

by flash chromatography for determining yields. Alternatively the crude mixture was treated in order to synthesize the correlation compounds without altering the isomer ratios.

^{1}H NMR Determination of the Enolate Geometry. - Alkenyloxy dialkoxyboranes from phenyl thiopropionate were generated in the NMR tube at temperatures ranging from -78°C to RT, using CD_2Cl_2 or $CDCl_3$ as solvent, and DPEA as base.
Z (1) δ: 5.59 (CH=C,q, J=6.96Hz); 1.70 (Me-C=C, d, J=6.96Hz).
E-(2) δ: 5.44 (CH=C,q, J=6.91Hz); 1.55(Me-C=C, d, J=6.91Hz).

Reaction with Benzaldehyde.- The ratios were determined by ^{1}H NMR and by HPLC. δ($CDCl_3$): 5.14 (CHO, syn, d, J=4.40Hz); 4.84 (CHO, anti,d, J=8.30Hz).
HPLC, silica gel 10μm, 4.6x250 mm column, eluant n-hexane-AcOEt 93:7, 2 ml/min: syn 13 min; anti 16 min.

Reactions with n-C_5H_{11}CHO.- The ratios were determined by HPLC and by ^{1}H NMR. δ ($CDCl_3$): 3.97 (CHO, syn, m); 3.75 (CHO, anti, m). HPLC,eluant n-hexane-AcOEt 9:1, anti 5 min; syn 6 min. Preparative HPLC of a mixture of aldol products generated by lithium enolate condensation provided compounds for which assignments for the ^{1}H NMR spectra were made by a comparison of the carbinol protons: δ ($CDCl_3$) 3.97 (syn,m, J=3.3Hz); 3.75 (anti, m, J=6.6Hz). The coupling constants were determined by an analysis of the signal of the proton on carbon 2.

Reactions with Chiral Aldehydes.

Entry 1.

The crude condensation product was analyzed by HPLC (n-hexane-AcOEt 97:3): anti 5 min, syn 8 min, syn-anti ≥ 20:1. The anti compound was isolated by flash chromatography (n-hexane-AcOEt 85:15) and characterized by ^{1}H NMR δ ($CDCl_3$-D_2O): 1.34 (3H, d, J=7.45Hz); 1.37 (3H, d, J=7.18Hz), 2.49-3.07 (3H, m), 3.70 (1H, dd, J=4.65, 7.67), 7.30 (5H,s), 7.42(5H,s).

The anti compound was then reduced ($LiAlH_4$, Et_2O) to give the Cram, anti diol (see ref.19); ^{1}H NMR δ($CDCl_3$): 0.98 (3H, d, J=6.90Hz), 1.30 (3H,d, J=7.20Hz), 1.52-2.03 (1H,m), 2.62 (2H,bs), 2.84-3.16 (1H,m), 3.44-3.86 (3H,m), 7.13-7.38 (5H,m).

The syn compound was isolated by flash chromatography (n-hexane-AcOEt 85:15) and characterized by ^{1}H and ^{13}C NMR. ^{1}H NMR δ($CDCl_3$-D_2O): 1.29 (3H, d, J=6.6Hz), 1.41 (3H, d, J=6.6Hz), 2.49-3.03 (2H,m), 4.16 (1H, dd, J=9.3,3.2Hz), 7.23-7.48 (10H,m). ^{13}C NMR selected values, δ($CDCl_3$): 10.9 (Me, major), 11.4 (Me, minor), 18.2 (Me, major), 18.4 (Me, minor), 43.0 (CH, major), 43.2 (CH, minor), 75.7 (CHO,minor), 76.0 (CHO, major). In this way a Cram-syn/AntiCram-syn ratio 8.2:1 was determined. This mixture was then hydrolized ($HgCl_2$, CH_3CN-H_2O 4:1, 2h, 80°C) to give the corresponding acids (see ref.17), which were isolated and characterized by ^{1}H and ^{13}C NMR. ^{1}H NMR δ($CDCl_3$): 1.18 (3H,d, J=7.2Hz), 1.36 (3H, d, J=6.9Hz), 2.20-2.51 (1H,m), 2.63-2.99 (1H,m), 4.17 (1H, dd, J=2.9, 9.2Hz), 6.25-6.70 (2H,bs), 7.10 - 7.25 (5H,m). ^{13}C NMR selected values δ(CD_3COCD_3): 10.1 (Me, major), 11.5 (Me, minor), 18.6 (Me, major), 19.3 (Me, minor), 76.3 (CHO, minor), 76.5 (CHO, major). In this way the major isomer was identified as Cram-syn, and the Cram-syn/AntiCram-syn ratio was confirmed (8.2:1). The mixture was also reduced ($LiAlH_4$-Et_2O) to give the corresponding diols (see ref.17,19), and the major compound was confirmed as the Cram-syn isomer by ^{1}H NMR δ($CDCl_3$): 0.94 (3H,d, J=6.6Hz), 1.36 (3H, d, J=6.6Hz), 1.4 (1H,m), 2.26 (2H,bs), 2.63-3.02 (1H,m), 2.63 (2H,d, J=4.8Hz), 3.97 (1H, dd, J=2.0,9.6Hz), 7.18-7.31 (5H,m).

Entry 2.

The crude condensation product was treated with $HgCl_2$ (CH_3CN-H_2O 4:1, 30 min, 80°C) to give the lactones. The ratio (1.1:1) was determined by capillary VPC (OV1; 60-100°C). The compounds were isolated by flash chromatography (n-hexane-AcOEt 15:85) and characterized by ^{1}H NMR. Felkin δ($CDCl_3$-C_6D_6): 1.3 (3H, d, J=6.7Hz), 2.45 (1H, dd, J=17.0, 4.0), 2.85 (1H, dd, J=17.0, 6.7), 2.9 (1H,bs), 4.15 (1H,m), 4.40(1H, dq, J=6.7,2.7Hz). CyclicCram δ($CDCl_3$-C_6D_6): 1.42 (3H, d, J=6.7Hz), 2.30 (1H,bs), 2.50 (1H, dd, J=17.0,1.0Hz), 2.85 (1H, dd, J=17.0,5.3Hz), 4.30-4.90 (2H,m).

Entry 3.

The crude condensation product was treated with $HgCl_2$ (see entry 2) to give the lactones. The ratio (2:1) was determined by capillary VPC (OV1;60-100°C). The compounds were isolated by flash chromatography (n-hexane-AcOEt 1:1) and characterized by ^{1}H NMR (see ref 16). Felkin-syn δ ($CDCl_3$): 1.30 (3H, d, J=7.0Hz), 1.46 (3H, d, J=6.6Hz), 2.57 (1H, dq, J=7.0, 9.0Hz), 3.67 (1H, dd, J=7.4, 9.0Hz) , 3.70 (1H, bs), 4.2 (1H, dq, J=7.4, 6.6Hz). CyclicCram-syn δ ($CDCl_3$): 1.30 (3H, d, J=8.0Hz), 1.38 (3H, d, J=6.7Hz), 2.05 (1H, bs), 4.15 (1H, t, J=5.0Hz), 4.60 (1H, m).

Entry 4.

The crude condensation product was treated with $HgCl_2$ (see entry 2) to give the lactones. The ratio (2.5:1) was determined by capillary VPC (OV1; 100-200°C). The compounds were isolated by flash chromatography (n-hexane-AcOEt 60:40) and characterized by ^{1}H NMR (see ref. 16,17,25). Felkin-syn δ ($CDCl_3$): 0.95 (3H, m), 1.00-2.00 (6H, m), 1.40 (3H, d, J=6.0Hz), 2.6 (1H, m), 3.8 (1H, dd, J=8.0,7.5Hz), 3.70 (1H, bs), 4.20 (1H, dq, J=7.5,6.0Hz); $[\alpha]_D^{20}$ =-17.5° (c 1.05, MeOH) (see ref. 25). CyclicCram-syn δ ($CDCl_3$): 0.95 (3H, m), 1.0-2.0 (6H, m), 1.36 (3H, d, J=6.7 Hz), 2.50 (1H, m), 4.15 (1H, bs), 4.18 (1H, dd, J=3.4,5.0Hz), 4.73 (1H, dq, J= 6.7,5.0Hz).

Entry 5.

The crude condensation product was analyzed by ^{1}H and ^{13}C NMR. ^{1}H-NMR δ ($CDCl_3$): 1.36 (3H, s), 1.43 (3H, s), 2.74-3.10 (3H, m), 3.90-4.12 (4H, m), 7.40 (5H, s). ^{13}C-NMR selected values δ ($CDCl_3$): 25.2 (Me, major), 26.4 (Me, minor), 46.8 (CH_2, major), 47.1 (CH_2, minor), 65.6 (CH_2O, minor), 66.6 (CH_2O, major), 68.5 (CHOH, minor), 69.7 (CHOH, major). In this way a Felkin/CyclicCram ratio ≥ 4:1 was determined. This mixture was then reduced ($LiAlH_4$, Et_2O) to give the corresponding diols (see ref 16,17). ^{1}H NMR δ ($CDCl_3$): 1.30 (3H, s), 1.38 (3H, s), 1.50-1.82 (2H, m), 3.18 (1H, bs), 3.42 (1H, bs), 3.66-4.04 (6H, m). ^{13}C-NMR selected values δ ($CDCl_3$): 34.8 (CH_2, major), 35.2 (CH_2,minor) , 60.1 CH_2OH, minor), 60.8 (CH_2OH, major), 65.7 (CH_2O, major), 65.9 (CH_2O, minor), 78.5

(CHO, major), 79.0 (CHO, minor), 109.1 (major), 109.5 (minor). In this way the isomers were identified as Felkin (major), and CyclicCram (minor) and the ratio was confirmed ($\geq$ 4:1).

Entry 6.

The crude condensation product was analyzed by ^1H and ^{13}C NMR. ^1H NMR $\delta(CDCl_3)$: 1.33(3H,d,J=6.9), 1.35(3H,s), 1.45(3H,s), 2.50-2.63(1H,bs), 2.90-3.24(1H,m), 3.80-4.28(4H,m), 7.40(5H,s). ^{13}C NMR selected values $\delta(CDCl_3)$: 25.2 (Me,major), 26.3(Me,minor), 49.4(CH,major), 51.8(CH,minor), 66.1(CH_2O,minor), 66.9(CH_2O,major), 71.9(CHOH,minor), 72.4(CHOH,major), 109.2(major), 109.4(minor). In this way a Felkin-syn/CyclicCram-syn ratio $\geq$ 7:1 was determined. This mixture was then reduced ($LiAlH_4$, Et_2O) to give the corresponding diols (see ref. 16,17). ^1H NMR δ ($CDCl_3$): 0.98(3H,d,J=7.2), 1.34(3H,s), 1.38(3H,s), 1.54(1H,s), 1.65-2.09(1H,m), 2.45(1H,d,J=3.3), 3.59-4.20(6H,m). ^{13}C NMR selected values $\delta(CDCl_3)$: 10.5(Me,major), 10.7(Me,minor), 73.3(CHOH,minor), 74.4(CHOH,major), 76.5(CHO,major), 77.0(CHO,minor), 108.8(major), 109.5(minor). In this way the isomers were identified as Felkin-syn (major) and CyclicCram-syn (minor) and the ratio ($\geq$ 7:1) was confirmed.

Entry 7.

The crude condensation product was treated with a catalytic amount of CF_3COOH in CH_2Cl_2. One of the two isomers instantaneously lactonized. The ratio was determined by HPLC (n-hexane-EtOAc 80:20). Cram-syn (methylester) 6.4 min; AntiCram-syn (lactone) 10.3 min. Cram-syn/AntiCram-syn ca.1:1. The lactone was characterized by ^1H and ^{13}C NMR (see ref. 9,20,21,22,23,24). $\delta(CDCl_3)$ 1.07(3H,d,J=5.3), 1.30 (3H,d,J=6.7), 1.55-2.10(3H,m), 2.44-2.66(2H,m), 2.82-3.13(1H,m), 4.51(1H,dd,J=4.2, 8.9), 7.4(5H,s). ^{13}C NMR selected values $\delta(CDCl_3)$: 10.7, 17.3, 27.2, 29.0, 30.2, 50.3, 84.9, 129.0, 129.3, 134.5.

Entry 8.

The crude condensation product was analyzed by HPLC (n-hexane-EtOAc 9:1): the AntiCram-anti isomer (7.5 min) was 55% of the mixture of the reaction products. The isomers were separated by flash-chromatography (n-hexane-EtOAc 85:15) and separately reduced ($LiAlH_4$-Et_2O). The major isomer (AntiCram-anti) was characterized by ^1H NMR (see ref. 14): δ ($CDCl_3$) 0.96 (3H,d,J=6.6), 1.08(3H,d,J=6.6), 1.69-2.10(2H,m), 2.10-2.35(2H,bs), 3.44(2H,d,J=5.2), 3.62(2H,d,J=5.06), 3.73 (1H,t,J=5.3), 7.3(5H,s). $\delta(C_6D_6)$ 1.0(3H,d,J=6.6), 1.09(3H,d,J=6.6), 1.60-2.12 (4H,m), 3.28(2H,d,J=5.31), 3.43(2H,d,J=5.3), 3.73(1H,t,J=5.3), 7.3(5H,s). The other diols (33% and 12% of the mixture of the reaction products) could not be unambiguously assigned by correlation, because the ^1H-NMR data are very similar one to another (see ref. 14).

All the remaining spectral and microanalytical data for the compounds synthesized were in agreement with the reported values (see ref. 9,14,16-25).

ACKNOWLEDGMENT

We wish to thank the Ministero della Pubblica Istruzione for financial support.

NOTES AND REFERENCES

1. Nomenclature: the use of the terms borate ester, borinic ester, and boronic ester is outmoded and scientifically confusing. In this paper we use: R_3B= trialkylborane, $ROBR_2$= alkoxy dialkylborane, $(RO)_2BR$= alkyl dialkoxyborane, $(RO)_3B$ trialkoxyborane. For sake of simplicity we use the name ethylene chloroboronate (ECB) instead of the IUPAC name 2-chloro-1,3,2-dioxaborolane.
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6. Nomenclature: the E-Z convention used in this paper is the regular C.I.P.-IUPAC convention. Thioester enolates have been nomenclated in this regular way by Masamune (ref.8,9), and in the opposite way by Evans (ref.8,10).
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