erythro-Selective Aldol Condensation *via* Triphenyltin Enolates. Stereoselection Independent of the Stereochemistry of the Enolates

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Summary Triphenyltin enolates, prepared from lithium enolates and triphenyltin chloride, undergo a rapid aldol condensation with aldehydes without the need for the presence of Lewis acids to give predominantly the *erythro*-product regardless of the geometry of the starting enolates.

THE recent widespread interest in stereoselective processes *via* aldol condensation[1] aroused our curiosity as to the stereochemical aspects of tin enolates. It is generally believed that, for kinetically controlled reactions, the *erythro*-product is favoured from *Z*-enolates, while the *threo*-product usually predominates from *E*-enolates.[1–3] Under thermodynamic control, the *threo*-isomer is the preferred product irrespective of the geometry of the starting enolates. We recently reported a new approach to *erythro*-selective coupling *via* the Lewis acid-mediated addition of crotyltrialkyltin to aldehydes, where the crotyl unit compounds may be either *cis* or *trans*.[4,5] This result suggested that a similar stereoselection may be achieved *via* certain tin enolates. To test this idea and to develop a new method for *erythro*-selective aldol condensation, we have

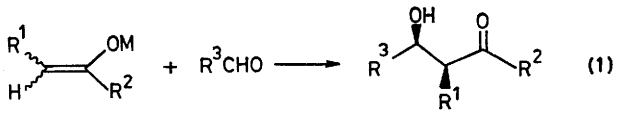
TABLE. *erythro*-selective aldol condensation *via* triphenyltin enolates.[a]

Entry	Enolate (1) R¹	R²	M	*E* : *Z*	R³ in R³CHO	% Yield of (2)[c] [*erythro* : *threo*][b]
1	Me	Et	$SnPh_3$[d]	8 : 92	Ph	80 [82 : 18]
2	"	"	"[d]	86 : 14	"	80 [74 : 26]
3	"	"	$SnBu^n_3$[d]	"	"	(92) [46 : 54]
4	"	"	$SnMe_3$[d]	"	"	(90) [47 : 53]
5	"	"	Li[d]	"	"	(30) [30 : 70]
6	$-[CH_2]_4-$		$SnPh_3$	—	"	80 [71 : 29]
7	$-[CH_2]_3-$		"[d]	—	"	92 [85 : 15]
8	Me	Et	"[d]	86 : 14	Bu^n	82 [66 : 34]
9	"	"	"[d]	8 : 92	"	85 [70 : 30]

[a] All reactions were carried out on a 1 mmol scale. Tin enolates were prepared by the addition of a THF solution of Ph_3SnCl or Me_3SnCl (1 mmol) to a THF solution of lithium enolates at −78 °C. Bu^n_3SnCl was added directly. Aldehydes were then added and the reaction was quenched with MeOH–H_2O after 30 min at −70 °C. [b] Determined by ^1H n.m.r. spectroscopy for entries 1—7, and by g.l.c. for entries 8 and 9. [c] Isolated yield in parentheses. [d] The lithium enolate was prepared *via* deprotonation of the corresponding ketone using LiTMP (lithium 2,2,6,6-tetramethylpiperidide) (Z. A. Fataftah, I. E. Kopka, and M. W. Rathke, *J. Am. Chem. Soc.*, 1980, **102**, 3959). Other lithium enolates were generated with Pr^i_2NLi. We assume that the *E* : *Z* ratio does not change during the formation of the tin enolate.

examined the reaction of various tin enolates with aldehydes.

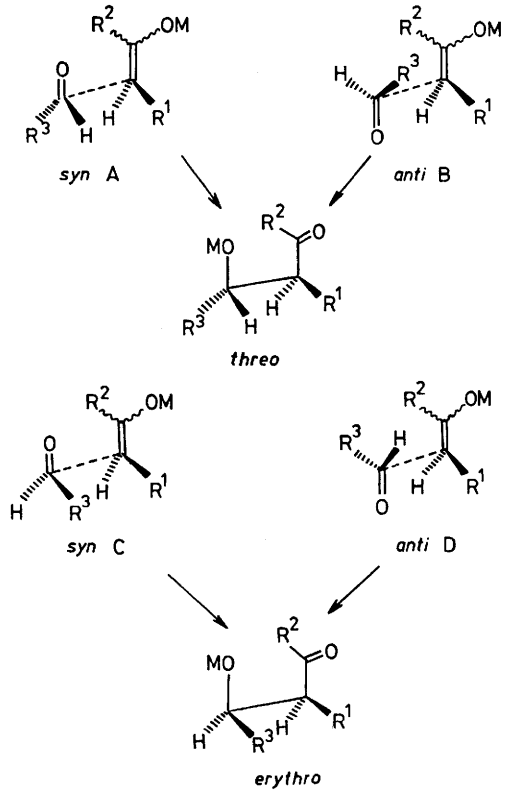
The results (Table) show that triphenyltin enolates, prepared from lithium enolates and triphenyltin chloride in tetrahydrofuran (THF) at −78 °C, undergo a rapid aldol condensation with aldehydes without assistance from Lewis acids to give predominantly the *erythro*-products regardless of the geometry of the starting enolates [reaction (1)].



(1) (2) (1)

It may be argued that the geometrical integrity of the starting enolates disappears during the reaction with triphenyltin chloride to give predominantly the *Z*-triphenyltin enolates. However, the results of entries 6 and 7 clearly exclude such a possibility, since the cyclohexenyl and cyclopentenyl enolates with fixed *E*-geometry afford predominantly the *erythro*-products. The fact that Lewis acids are not required is an important aspect of the process, since reactions of lithium enolates occur under basic conditions.

The present results cannot be explained by a conventional cyclic transition state. We propose an acyclic transition state, as previously suggested by us[4] and others[3,6] (Scheme).† It is clear that configuration *anti* D leading to the *erythro*-product is favoured for steric reasons, and the geometry of the enolates is not important for the stereoselective reaction. Presumably, the reaction of tributyl and trimethyltin enolates (entries 3 and 4) proceeds *via* a more or less cyclic mechanism.



SCHEME. Acyclic transition state.

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† We make the assumption that the reaction proceeds through an enolate form rather than the α-metallaketone form.

[1] For a review, see P. A. Bartlett, *Tetrahedron*, 1980, **36**, 3.
[2] For example, C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, and J. Lampe, *J. Org. Chem.*, 1980, **45**, 1066; D. A. Evans, E. Vogel, and J. V. Nelson, *J. Am. Chem. Soc.*, 1979, **101**, 6120; A. I. Meyers and P. J. Reider, *ibid.*, 1979, **101**, 2501; I. Kuwajima and E. Nakamura, *ibid.*, 1975, **97**, 3257; K. Maruoka, S. Hashimoto, Y. Kitagawa, H. Yamamoto, and H. Nozaki, *ibid.*, 1977, **99**, 7705; S. Masamune, *Aldrichimica Acta*, 1978, **11**, 23; T. Inoue and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 174; P. Fellmann and J.-E. Dubois, *Tetrahedron*, 1978, **34**, 1349.
[3] S. Murata, M. Suzuki, and R. Noyori, *J. Am. Chem. Soc.*, 1980, **102**, 3248.
[4] Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, *J. Am. Chem. Soc.*, 1980, **102**, 7107; Y. Yamamoto and K. Maruyama, *Tetrahedron Lett.*, 1980, 4607.
[5] H. Yatagai, Y. Yamamoto, and K. Maruyama, *J. Am. Chem. Soc.*, 1980, **102**, 4548.
[6] J. Mulzer, G. Bruntrup, J. Finke, and M. Zippel, *J. Am. Chem. Soc.*, 1979, **101**, 7723.