

Table I. Chiral *threo*- β -Hydroxy Esters **3** via Boron Azaenolate **1**

RCHO	<i>threo</i> : <i>erythro</i> , ^a %	<i>threo</i> - 3 , ^{d,e} % ee	$[\alpha]_D^{CHCl_3}$ f (c)	3 , overall ^g yield, %
EtCHO	92:8	77	-9.9 (1.3)	26
PrCHO	91:9	77	-2.5 (1.0)	22
<i>n</i> -PentCHO ^h	90:10 ^b	77	-3.1 (1.2)	25
Me ₂ CHCHO	91:9	85	-12.5 (1.0)	36
<i>c</i> -HexCHO ^h	95:5	84	-8.1 (1.0)	31
<i>t</i> -BuCHO	94:6 ^c	79	-21.2 (1.0)	29

^a Determined by GLC with base line separation of both peaks (35% DEGS; 1-m column; 140–200 °C; He flow, 40 mL/min. ^b Separation of peaks was >85%, prohibiting exact ratio determination. ^c Complete peak separations were accomplished by using 10% SE-30 at 110 °C. ^d Determined by chiral shift reagent tris[3-(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium III using 10 mg of LISR and 10 mg of GLC purified methyl ester **3** in 0.4 mL of CDCl₃ on a Varian T-60 instrument. The OCH₃ signal was completely separated and integrated at \sim 4.08 (major) and \sim 4.13 (minor). Slight variations in chemical shifts were noted for each compound. ^e Absolute configurations are *2R,3R* except for last entry which is *2R,3S* due to priority change. ^f Rotations for pure *threo* products after purification by VPC. ^g Yields based on diisopinocampheylborane and the subsequent five steps to **3**. Due to the instability of the borane triflate⁴ and the boron enolate **1**, it is not currently possible to assess the yields of each individual step, only the overall yield of **3**. Improvements toward this end are in progress. ^h Pent, pentyl; *c*-Hex, cyclohexyl.

Table II. Chiral *Erythro*- β -Hydroxy Esters **4** from Boron Azaenolate **2**

RCHO	<i>erythro</i> : <i>threo</i> , ^a %	<i>erythro</i> - 4 , % ee ^b	config ^c	$[\alpha]_D^{CHCl_3}$ f (c)	overall yield, %
EtCHO	98:2	40	<i>2S,3R</i>	1.4 (2.7)	44
Me ₂ CHCHO	98:2	41	<i>2S,3R</i> ^d	-2.3 (2.4)	42
<i>t</i> -BuCHO	97:3	60	<i>2S,3S</i> ^e	-6.6 (2.1)	50

^a Determined by GLC as described in Table I. ^b These were determined by using the chiral shift reagents (Table I) without exclusion of the *threo* product. ^c Configuration assigned by similarity in shifts using chiral shift reagent. The CCH₃ doublet of the major enantiomer always appeared at lower field than the minor one. ^d Based on reported configuration of (+)-(*2R,3S*),¹ ^e Assigned with the same sense of configuration as other cases; however, a priority change results in *S* for the β carbon. ^f Rotations include the 2–3% of *threo* product.

whereas **6c** and **6d** were (–) and (+)-*erythro*-**4**, confirmed by comparison with (+)-(*2R,3S*)-**4** prepared by Evans.^{1k} The *threo* pair **6a** and **6b** were identified with regard to their absolute configuration by epimerization at C-2. Thus, **6a** was treated with 2.0 equiv of *tert*-butyllithium (–78 °C, THF) and then quenched with acetic acid. HPLC analysis (silica gel) showed a mixture of **6a** and **6c**, indicating they now differed only at C-2. Similarly, **6b** was epimerized to a mixture of **6b** and **6d**. These studies confirm the relationship between **6a–d**, and their absolute configurations are indicated.

The use of boron azaenolate **2**, wherein the oxazoline ring represents the chiral auxiliary and boron contains the achiral bicyclo system (9-borabicyclononane), gave mainly the *erythro*- β -hydroxy esters **4** upon reaction with several aldehydes. Although the diastereoselection was quite high, the enantioselection was only moderate (Table II). The complexities of this process are currently outside the realm of our complete understanding due partially to the fact that the geometry of the azaenolates **1** and **2** are not known. It is known, however, that at the conditions of their formation, kinetically generated from a dialkylboryl triflates, they produce only a single species. This was confirmed by ¹³C NMR spectroscopy of the enriched methyl group⁸ (\sim 50% ¹³C) on the olefin in **2** which showed only a single signal at temperatures from –78 to –25 °C. Equilibration was effected by prolonged stirring of **2** (3 h) at room temperature which showed a steady increase of a second methyl signal finally reaching a ratio of 2:1. Despite the single azaenolate **2** at temperatures where the aldol was normally run, the % ee of *erythro* product was only 40–60%. Thus, there appears at this time that there is little correlation between the population of the azaenolates and the enantioselectivity observed. The other factor contributing to our lack of understanding of this process is the nature of the transition states. The aldol transition states proposed by Zimmerman⁹ and employed

by others¹⁰ do not seem to give a clear indication of the process, and it has been suggested¹¹ that “boatlike” rather than “chairlike” transition states should also be considered. We continue to probe this interesting yet mystifying process.¹²

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Supplementary Material Available: Methods of purification, $[\alpha]_D$ values, and IR and NMR data for the hydroxy esters (2 pages). Ordering information is given on any current masthead page.

(10) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. Evans, D. A.; Taber, T. R. *Tetrahedron Lett.* **1980**, *21*, 4675.

(11) We thank Professor David Evans for discussion on this matter.

(12) Additional data pertaining to the β -hydroxy esters reported herein are given as supplementary material.

Polymerized Microemulsions

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Emulsion polymerization has been the focus of intensive investigative efforts since its discovery by Harkins.¹ Such polymerizations are characterized by rapid rates of polymerization that culminate in the production of high molecular weight polymer

(7) (a) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. (b) Meyers, A. I.; Reider, P. J. *Ibid.* **1979**, *101*, 2501. (c) Buse, C. T.; Heathcock, C. H. *Ibid.* **1977**, *99*, 8109.

(8) Meyers, A. I.; Synder, E. S.; Ackerman, J. J. H. *J. Am. Chem. Soc.* **1978**, *100*, 8186.

(9) Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920.

(1) (a) H. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947); (b) W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948); (c) D. C. Blackley, “Emulsion Polymerization”, Applied Science, London, 1975; (d) S. W. Landowne, R. G. Gilbert, D. H. Napper, and D. F. Sangster, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1344 (1980).

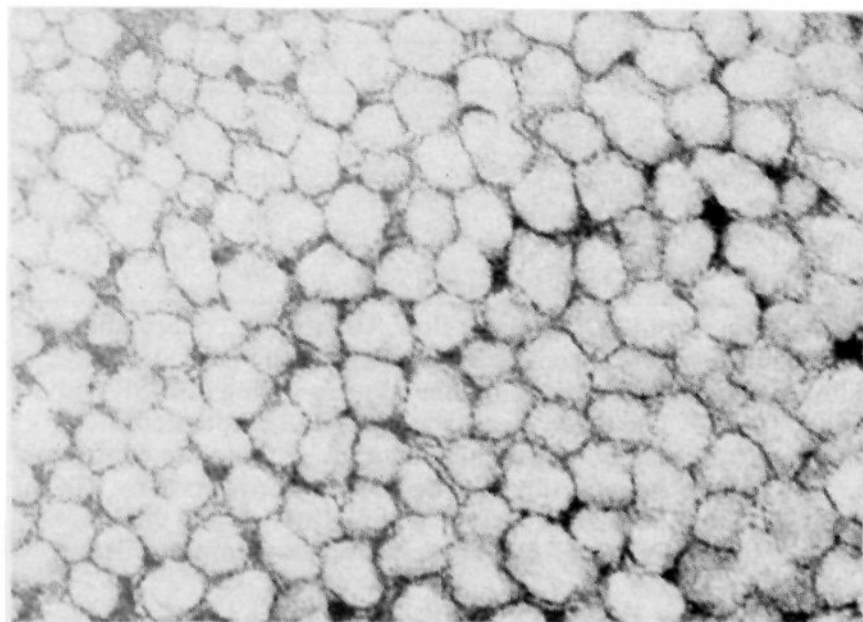


Figure 1. Electron micrograph of radiation polymerized styrene microemulsion (250 000 \times).

latex particles (>1000 Å in diameter). This is a consequence of the isolation of single free radicals that polymerize in loci of small dimensions where the normal termination reactions are less important.

We wish to report here the first account of a *microemulsion* polymerization that produces spherical latex particles ranging in size from 200 to 400 Å in diameter. An oil in water microemulsion (μ E) consisting of 1.0 g of cetyltrimethylammonium bromide (CTAB), 1.0 g of styrene, and 0.5 g of hexanol in 50 mL of water was prepared and polymerized by two conventional methods: (a) thermally (60 °C) by use of 1.0×10^{-6} M AIBN and (b) radiolytically by use of a Cs γ -ray source. These two different polymerization techniques afforded monodisperse latex particles of diameters 350 ± 30 and 200 ± 20 Å, respectively. Figure 1 shows an electron microscopic picture of a styrene μ E polymerized by method b. The number average diameter of the polymer lattices were measured from the electron photomicrograph according to the expression

$$\bar{D} = \frac{\sum_i \chi_i D_i}{\sum_i \chi_i}$$

where χ_i is the fraction of particles having a diameter D_i . The particle size of 210 Å determined by this method was found to be in good agreement with that obtained by Nicomp particle analyzer.

The polymerized particles differed from micelles or microemulsions in providing two unique sites for location of reacting molecules. Neutral, water insoluble molecules such as pyrene P, when added to the polymerized μ E, are found to partition between the polymer matrix, where they are immobilized, and the surfactant spherical shell where the microenvironment is similar to

that of micelles. On the other hand, species bearing an opposite charge to that of the surfactant, such as pyrene sulfonic acid (PSA), are found to be completely adsorbed to the surface of the latex particle by simple electrostatic interactions. These two different modes of interactions are well exemplified by the quenching of P and PSA fluorescence by surface adsorbed quenchers such as I^- and cetylpyridinium chloride (CPC). The quenching of PSA fluorescence by I^- and CPC is rapid and quite similar in both micelles and polymerized particles. With pyrene, however, an initial rapid quenching is observed for about 20% of the fluorescence, the remaining 80% being unaffected.² The III/I₁ ratio of 0.95 of the unquenched fluorescence shows that this component is in a more hydrophobic environment than the 20% quenched component, III/I₁ = 0.76.³ This suggests that pyrene experiences two sites of solubilization, one accessible to ionic surface quenchers, i.e., the surface, and the other inaccessible to these quenchers, i.e., the polymerized core, within the lifetime of its excited state. Under aerated conditions the decay of excited PSA is a single exponential with a lifetime τ of 50 ns, while excited pyrene shows a nonexponential decay that can be fitted well to a double exponential function

$$[P^*]_t/[P^*]_{t=0} = \alpha e^{-t/\tau_m} + (1 - \alpha)e^{-t/\tau_p}$$

where $\alpha = 0.20$ and $\tau_m = 230$ and $\tau_p = 425$ ns are the lifetimes of P^* solubilized in the micellar region and polymer matrix, respectively.

The polymerized microemulsions show additional advantageous features to simply dynamic micelles or microemulsions: the static quality of these systems enables one to investigate the structure by means of electron microscopy; it is possible to immobilize one reactant at the particle core and locate the other reactant at the particle surface. This is important in investigating spatial effects on photoinduced reactions. For example, electron transfer from surface located dimethylaniline (DMA) to core immobilized excited pyrene, P^* , takes place with kinetics which differ from those observed in micelles and fluid microemulsions. It is suggested that immobilization of the DMA/ P^* eliminates the diffusion processes observed in fluid systems, thus bringing into play electron transfer over large distances (20 Å). The systems thus enable one to assess the relative importance of diffusion and static processes in photochemical reactions.

A fuller report will be published at a later date.

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(2) The fact that similar results were obtained with a dialyzed μ E solution would tend to argue against the possibility raised by the referee that the partitioning may be occurring between polymer particles and free micelles.

(3) J. K. Thomas, *Chem. Rev.*, **80**, 283 (1980).

Book Reviews

Trace Metals in the Environment. Volume 5. Indium. By I. C. Smith, B. L. Carbon, and F. Hoffmeister (Midwest Research Institute). Ann Arbor Science Publishers, Ann Arbor, Michigan. 1978. xxi + 552 pp. \$24.

This volume is the fifth in a series which has discussed thallium, silver, zirconium, palladium, and osmium in the environment. It gives extensive, exemplified coverage of virtually every aspect of indium, with sections on uses, chemistry, geochemistry and occurrence, industrial processes as environmental sources, occurrence in living organisms, physiological effects, environmental losses, and health effects. Over 1100 references cover the range from historical aspects to literature appearing in 1978. An enormous amount of the relevant data has been presented in over 80 figures and tables throughout the text.

The large collection of data has allowed the authors to make many observations on indium inventories, particularly within the United States. Through the subject index and list of contents, specific information is quite accessible and the 15-page summary of all the areas covered gives a good overview of the major features treated in the text.

The book's size is a reflection of the very extensive literature survey, rather than of the importance of indium in the environment. Indeed, the research indicates that the consumption and release of indium are small and potential toxicity is generally masked by the copresence of other toxic elements in higher concentrations. The title of the book is a little misleading, since its major value will be as a source book for anyone working in any way with indium.

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