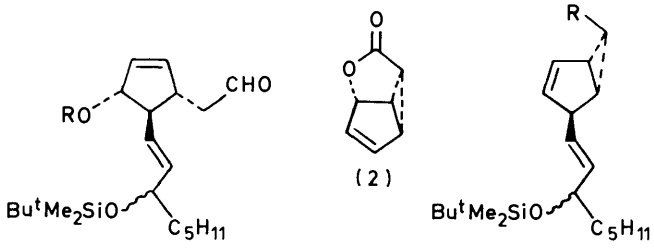
Stereochemistry of the Aldol Reaction between [4-t-Butyldimethylsilyloxy-5-(3-t-butyldimethylsilyloxyoct-1-enyl)-cyclopent-2-enyl]ethanal and Cyclopentanone Enolates; A Key Step in the Total Synthesis of Prostacyclin

Anthony D. Baxter, Stanley M. Roberts, Basil J. Wakefield, and Geoffrey T. Woolley
The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT
Roger F. Newton *
Chemical Research Department, Glaxo Group Research, Ware, Herts. SG12 0DJ

Reactions of lithium, boron, zirconium, and tin enolates derived from cyclopentanone with [4-t-butyldimethylsilyloxy-5-(3-t-butyldimethylsilyloxyoct-1-enyl)cyclopent-2-enyl]ethanal (6) gave mainly the 5*R*, 6*R*, and 5*S*, 6*S* (prostaglandin numbering), *threo*-adducts, regardless of the nature of the enolate; the highest yield of *threo*-products (83% of a total yield of 93%) was obtained with lithium enolate in pentane at −78 °C. In contrast, the ratio of 5*R*,6*R* to 5*S*,6*S* products was significantly affected by the nature of the enolate, ranging from *ca.* 1 : 1.3 with a boron enolate to *ca.* 1 : 3 with a tin enolate, and *ca.* 1 : 4 with a lithium enolate.

[5-(3-t-Butyldimethylsilyloxyoct-1-enyl)-4-hydroxycyclopent-2-enyl]ethanal (1)[1,2] † is a valuable intermediate for the synthesis of prostanoids, since it has the required stereochemistry and functionality about the cyclopentane ring, and the aldehyde function is available for the elaboration of the upper side-chain. For example, it has been converted into 6β-prostaglandin I_1[2] and 9-deoxa-9,10-didehydroprostaglandin D_2.[4] For the present work we have used the route to the aldehyde (1) described in ref. 1; it has proved to be capable of furnishing the compound in gram quantities. The least reliable stage was the reaction of the tricyclic lactone (2) with the side-chain cuprate reagent in the presence of hexamethylphosphorous triamide (HMPT), which occasionally gave the amide (3) as well as the required acid (4). However, the amide (3) could be converted directly into the aldehyde (5) by reduction with di-isobutylaluminium hydride.



(1) R = H
(6) R = Bu^tMe_2Si

(3) R = $CONMe_2$
(4) R = CO_2H
(5) R = CHO

Our route for the synthesis of prostacyclin methyl ester from the silylated derivative (6) of the hydroxyaldehyde (1) is outlined in Scheme 1.[5] In this synthesis, the stereochemistry of the aldol reaction is crucial. Most importantly, as a consequence of the *trans*-elimination in the last step leading to prostacyclin methyl ester, only the *threo*-isomers (7) and (8) can give the required *E*-geometry at the Δ^5 double bond; the *erythro*-isomers (9) and (10) will give the *Z*-isomer. Furthermore, the ease of halocyclisation is greatly dependent on the stereochemistry of the aldol products. In a similar case, reported earlier, the 6(*S*)-isomer (12) cyclised much more slowly than its 6(*R*)-epimer.[2]

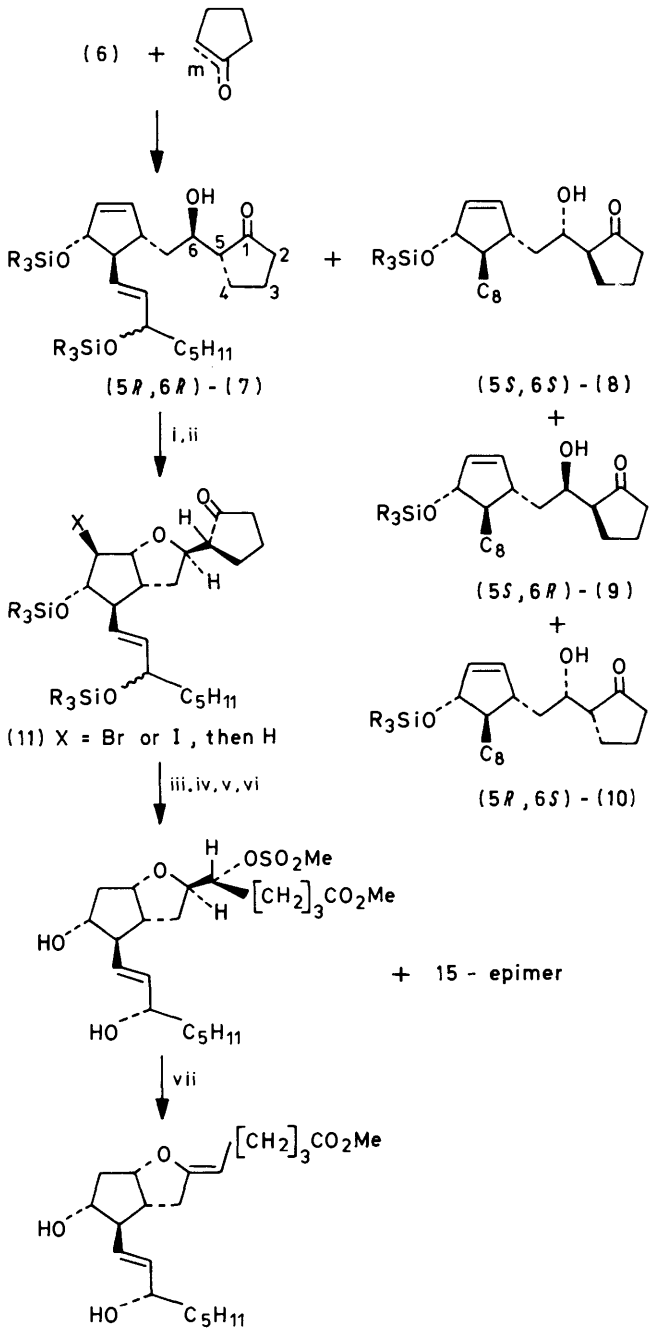
Our initial experiments were made with the lithium enolate of cyclopentanone, and gave four aldol products, as expected, together with small amounts of the self-condensation product of cyclopentanone. T.l.c. on silica (5% ethyl acetate: 95% chloroform) showed the aldol products grouped as two pairs (R_F 0.76 and 0.72; and 0.42 and 0.32). On the evidence of n.m.r. spectroscopy, the first pair were judged to be the *threo*-isomers and the second pair the *erythro*-isomers. Thus, the signals for the C*H*OH proton occurred at δ 3.84 and 3.76, for the *threo*-isomers and δ 4.27 and 4.20, for the *erythro*-isomers. The chemical shifts for this proton in the known[10] *threo*- and *erythro*-adducts of cyclopentanone enolate with benzaldehyde occurred at δ 4.75 and 5.25 respectively.

These assignments were later confirmed by the conversion of both the *threo*-isomers (7) and (8) into prostacyclin methyl ester.[5,6] In our initial experiments we discovered that only one of the *threo*-isomers underwent iodocyclisation, to the iodo-compound (11; X = I).[5] By analogy with the earlier case, we suggest that it was compound (7) (stereochemistry 5*R*,6*R* using prostaglandin numbering and designated β for convenience), which cyclised.

In this paper we describe and discuss the stereochemistry of the reaction of the aldehyde (6) with a variety of cyclopentanone enolates. Our results are summarised in the Table. These results display two striking features: the comparative lack of sensitivity of the *threo*/*erythro* ratio to the nature of the enolate, but the large variation in the ratio of components within each diastereoisomeric pair.

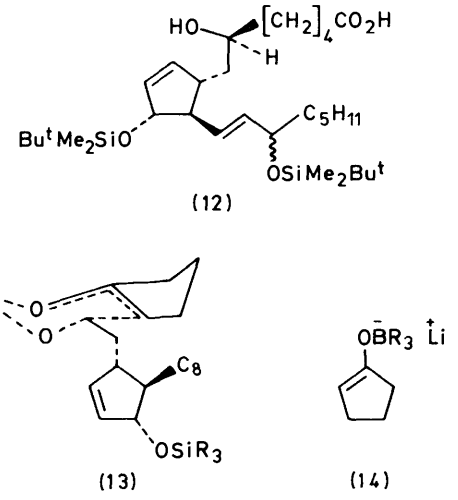
In various studies of the reactions of enolates with simple aldehydes, very high degrees of *threo*- or *erythro*-selectivity have been observed in certain cases.[7] Various hypotheses have been advanced to account for this stereoselectivity,[7a,8] but it seems clear that energy differences between the transition states must be small, so that while they are significant in simple cases, they may be outweighed by other steric constraints for more complex systems. In our case, the reaction is apparently inherently *threo*-selective (compare our entry 1,

† The analogous tetrahydropyranyl-protected aldehyde has also been prepared by a multi-step synthesis from 7-benzyloxymethylnorborn-5-en-2-one.[3]



Scheme. *Reagents:* i, X^+; ii, Bu_3SnH; iii, *m*-$ClC_6H_4CO_3H$; iv, K_2CO_3–MeOH; v, $MeSO_2Cl$–Et_3N; vi, $MeCO_2H$–THF–H_2O; vii, DBU

Table, with the corresponding reaction with benzaldehyde, which gives little or no stereoselection [9]). This selectivity could be explained in terms of a Zimmerman-Heathcock transition state for the formation of the *threo*-aldol such as (13) in which all the bulky groups lie at equatorial positions to the pseudo-chair ring. However, in the absence of a detailed knowledge of the preferred conformations of the aldehyde (6) or of the mechanism of the reaction we prefer simply to accept the *threo*-selectivity as an empirical fact. Some variation from the ' natural ' ratio is observed with enolates that have been reported to be *erythro*-selective (Table, entries 4, 7, 8), notably the zirconium and tin enolates (*cf.* refs. 10, 11). As a variation on the simple boron enolate [8a,*] (entry 4) we tried the ' ate complexes ' (14), in which the negative charge is presumably largely localised on boron. These gave somewhat less *erythro*-products than the dialkylboron enolate but such reagents are much more easily prepared and may be useful in simpler cases.*



The large variation in the ratios of the two *threo* diastereoisomers and the ratios of the two *erythro* diastereoisomers is perhaps even more surprising. Since the formyl group in (6) is not bonded to a chiral centre, generalisations such as Cram's rule are not strictly applicable, and little stereoselectivity would be predicted. For example, in recent experiments on the addition of Grignard reagents to *S*-(+)-3-methylpentanal, the maximum ratio of the products was 1 : 1.3.[12] However, although a similar ratio was observed between the two *threo*-isomers in the reaction of the aldehyde (6) with the dibutylboron enolate (Table, entry 4), with the lithium enolate in ether at −120 °C it was as high as 1 : 4.1 (entry 3). Once again, the variation in this ratio must be due to subtle steric factors.

For the purpose of the synthesis of prostacyclin, since the problem of the halocyclisation of the epimer (8) has now been overcome,[6] the optimum conditions are those of the Table, entry 2, *i.e.* lithium enolate in pentane at −78 °C, which give a 93% yield of aldol products, 83% of which have the required *threo*-configuration. Work is now in progress on epimerisation of the *erythro*-isomers, to enable all the aldol products to be utilised.

Experimental

Unless otherwise stated, ^1H n.m.r. data were recorded for solutions in deuteriochloroform with tetramethylsilane as external standard; i.r. spectra were recorded for neat films; mass spectra were determined after ionisation by electron impact at 70 eV (e.i.m.s.) or chemical ionisation using ammonia (c.i.m.s.); t.l.c. was carried out with Camlab Polygram pre-coated silica gel plates; column chromatography was carried out using medium pressure over silica (Merck Kieselgel, Art. 7 736; *ca.* 20 × weight of substrate); light petroleum refers to the fraction, b.p. 40—60 °C. All reactions involving

* Since the completion of our work, it has been noted that in the presence of an excess of trialkylboron, the reaction between benzaldehyde and cyclopentanone enolate becomes highly *threo*-selective: Y. Yamamoto, H. Yatagai, and K. Maruyama, *Tetrahedron Lett.*, 1982, **23**, 2387.

Table. Reaction of the aldehyde (6) with enolates of cyclopentanone

Metal counterion of enolate	Reaction temp. (°C)	Solvent	Total yield (%)	Product ratio (%) (7) : (8) : (9) : (10)	Total *threo*%
Li^+	−78	Et_2O	80	22 : 53 : 6 : 19	75
Li^+	−78	Pentane	93	26 : 57 : 4 : 13	83
Li^+	−120	Et_2O	92	15 : 62 : 3 : 19	77
BBu_2^s	−78	Et_2O	70	28 : 36 : 17 : 19	64
$BEt_3^-Li^+$	−78	Et_2O–THF	87	27 : 40 : 13 : 20	67
BBu_3^s–Li^+	−78	Et_2O–THF	72	23 : 49 : 6 : 22	72
Zr(cp)Cl	−78	THF	61	24 : 38 : 9 : 28	62
$SnPh_3$	−78	THF	78	14 : 48 : 10 : 28	62

organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen, using dried apparatus and solvents.

[5-(3-*t*-*Butyldimethylsilyloxyoct*-1-*enyl*)-4-*hydroxypent*-2-*enyl*]*ethanal* (1).—(*a*) The aldehyde (1) was prepared essentially as described in ref. 1*b*. On one occasion the reaction of 2-oxabicyclo[3.3.0.0^{4,6}]oct-7-en-3-one with the cuprate reagent (1.5 mol equiv.) derived from 1-iodo-3-t-butyldimethylsilyloxyoct-1-ene in the presence of HMPT (3.5 equiv.) gave, besides the acid (4) (12%), NN-*dimethyl*-4-exo-(3-*t*-*butyldimethylsilyloxyoct*-1-*enyl*)*bicyclo*[3.1.0]*hex*-2-*ene*-6-*carboxamide* (3) (42%); $\nu_{max.}$ 1 640 cm^{-1}; δ_H 0.0 (6 H, s, $SiMe_2$), 0.9 (12 H, m, $4CH_3$), 1.25 (8 H, m, $4CH_2$), 1.7—2.2 (2 H, m, 1-, 5-H), 2.4 (1 H, m, 6-H), 2.95 (3 H, s, NMe), 3.1 (3 H, s, NMe), 3.65 (1 H, m, 4-H), 4.0 (1 H, m; 3-H′), and 5.3—5.9 (4 H, m, 2-, 3-, 1′-, and 2′-H) [Found: (e.i.m.s) M^+, 391.2903. $C_{23}H_{41}NO_2Si$ requires M, 391.2904].

(*b*) A solution of di-isobutylaluminium hydride (M in hexane, 0.52 ml) was added dropwise during 30 min to a solution of the amide (3) (0.20 g, 0.55 mmol) described in (*a*) in light petroleum (7 ml) at −78 °C. The mixture was stirred at −78 °C for 1 h. Methanol (2 ml), water (20 ml), and 2M- hydrochloric acid (6 ml) were added. The organic layer was separated, and the aqueous phase was extracted with ether (3 × 50 ml). The combined organic layers were neutralised with 2M-sodium hydroxide and then re-extracted with ether (3 × 50 ml) Conventional work-up of the combined organic layers, followed by chromatography on silica, gave the bicyclic aldehyde (5) (116 mg, 66%), identical (i.r., n.m.r.) with the material previously described.[1b]

2-[4-*t*-*Butyldimethylsilyloxy*-5-(3-*t*-*butyldimethylsilyloxyoct*-1-*enyl*)*cyclopent*-2-*enyl*]*ethanal* (6).—To a solution of the aldehyde (1) (2.8 g) in DMF (100 ml) was added t-butylchlorodimethylsilane (2.34 g) and imidazole (2.34 g). The homogeneous mixture was set aside at room temperature for 15 h. Water (100 ml) was added, and the solution was extracted with ether (4 × 100 ml). Conventional work-up and chromatography (silica, 2% ethyl acetate in light petroleum) gave the *protected aldehyde* (6) (2.94 g, 80%), $\nu_{max.}$ 1 720 cm^{-1}; δ_H 0.0 (12 H, s, 2 $SiMe_2$), 0.7—1.0 (21 H, m, 7 Me), 1.05—1.6 (8 H, m, 4 × CH_2), 2.0—2.85 (4 H, m, 2-, 1′-, and 5′-H), 4.05 (1 H, m, 3‴-H), 4.50 (1 H, m, 4′-H), 5.35—5.6 (2 H, m, 1″- and 2″-H), 5.6—5.85 (2 H, s, 2′- and 3′-H), and 9.8 (1 H, t, J 1.5 Hz, CHO).

Reactions of [4-*t*-*Butyldimethylsilyloxy*-5-(3-*t*-*butyldimethylsilyloxyoct*-1-*enyl*)*cyclopent*-2-*enyl*]*ethanal* (6) *with Enolates of Cyclopentanone*.—The yields of the products of the reactions described below are recorded in the Table. The yields take into account recovered starting material. In each case a little of the self-condensation product of cyclopentanone was observed but was not recovered quantitatively.

(*a*) To a stirred solution of di-isopropylamine (39.5 mg, 0.39 mmol) in diethyl ether at 0 °C was added dropwise n-butyl-lithium (1.44M in hexane; 0.27 ml), the temperature being kept below 3 °C. The solution was stirred at 0 °C for 10 min, then cooled to −78 °C. Cyclopentanone (32 mg, 0.39 mmol) was added dropwise during 2 min, and the mixture was stirred at −78 °C for a further 10 min. A solution of the aldehyde (6) (185 mg, 0.376 mmol) in dry ether (3 ml) was added rapidly, and the mixture was stirred at −78 °C for 10 min. Saturated aqueous ammonium chloride (20 ml) was added, and the mixture was allowed to warm to room temperature. The mixture was extracted with diethyl ether (4 × 25 ml), and the combined extracts were washed with water (2 × 20 ml), dried ($MgSO_4$), filtered, and evaporated, to leave a yellow gum (0.21 g). The gum was subjected to repeated short-path column chromatography (silica, eluant 1% ethyl-acetate, 19% dichloromethane, 80% light petroleum, to afford the following. (i) threo-β-1-(2-*Oxocyclopentyl*)-2-[4-endo-*t*-*butyldimethylsilyloxy*-5-exo-(3-*t*-*butyldimethylsilyloxyoct*-1-*enyl*)*cyclopent*-2-*enyl*]*ethanol* (7) (30.4 mg), t.l.c. R_F 0.76 (5% ethyl acetate–5% dichloromethane); $\nu_{max.}$ 3 450 and 1 720 cm^{-1}; δ_H 0.0 (12 H, s, 2 × $SiMe_2$), 0.7—1.0 (21 H, m, 7 × Me), 1.0—2.5 (18 H), m, 2.62 (1 H, m, 1‴-H), 3.84 (1 H, tm, largest coupling 7 Hz, 1-H), 4.08 (1 H, m, 3″-H), 4.55 (1 H, t, J 7 Hz, 4′-H), 5.54 (2 H, m, 1″- or 2″-H), 5.70 (1 H, dm, largest coupling 5 Hz, 2′- or 3′-H), 5.95 (1 H, dm, largest coupling 5 Hz, 2′-H or 3′-H) [Found (e.i.m.s.) M^+ − 141, 423.2750. $C_{32}H_{60}O_4Si_2$ − C_5H_8O − C_4H_9 requires m/z 423.2748].

(ii) The threo-α-*isomer* (8) (74.5 mg); t.l.c. R_F 0.72; $\nu_{max.}$ 3 450, and 1 720 cm^{-1}; δ_H 0.0 (12 H, s), 0.7—1.0 (21 H, m), 1.0—2.4 (18 H, m), 2.55 (1 H, m, 1‴-H), 3.76 (1 H, tm, largest coupling 9 Hz, 1-H), 4.06 (1 H, q, 3″-H), 4.15 (1 H, m, OH), 4.50 (1 H, dd, J 10 Hz and 4.5 Hz, 4′-H), 5.56 (2 H, m, 1″- and 2′-H), 5.65 (1 H, m, 2′- or 3′-H), and 5.88 (1 H, d, J 5 Hz, 2′- or 3′-H) [Found (e.i.m.s.) M^+ − 141, 423.2750. $C_{32}H_{60}O_4Si_2$ − C_5H_8O − C_4H_9 requires m/z 423.2748].

(iii) The erythro-β-*isomer* (9) (8.5 mg); t.l.c. R_F 0.42; $\nu_{max.}$ 3 450 and 1 720 cm^{-1}; δ_H 0.034, 0.040, 0.053, 0.056, 0.062, 0.071, 0.073 (12 H total, 2 $SiMe_2$), 0.888, 0.890, 0.895, 0.898 (18 H total; 2 × Bu^t), 1.0—2.4 (21 H, m), 2.55 (1 H, m, 1‴-H), 4.07 (1 H, m, 3″-H), 4.27 (1 H, m, 1-H), 4.53 (1 H, m, 4′-H), 5.50 (1 H, m, 1″- or 2″-H), 5.53 (1 H, m, 1″- or 2-H), 5.69 (1 H, dq, J 6 Hz and 2 Hz, 2′- or 3′-H), 5.90 (1 H, m, 2′- or 3′-H); mass spectrum m/z 564 (M^+), 507 (M − C_4H_9), 423 (M − C_4H_9 − C_5H_8O) [Found: (e.i.m.s.): M^+, 564.4053. $C_{32}H_{60}O_4Si_2$ requires M, 564.4027].

(iv) The erythro-α-*isomer* (10) (26.3 mg); t.l.c., R_F 0.32 $\nu_{max.}$ 3 450 and 1 720 cm^{-1}; δ_H 0.031, 0.054, 0.062, 0.067, 0.073 (12 H total, 2 $SiMe_2$), 0.883, 0.892, 0.895 (18 H, total, 2 Bu^t), 1.00—2.35 (21 H, m), 2.42 (1 H, m, 1‴-H), 4.07 (1 H,

q, *J* 5 Hz, 3″-H), 4.2 (1 H, dq, *J* 9.5, 3.5 Hz, 1-H), 4.50 (1 H, dm, largest coupling 11 Hz, 4′-H), 5.6—5.45 (2 H, m, 1″- and 2′-H), 5.70 (1 H, tt, *J* 6.5, 2 Hz, 2′- or 3′-H), 5.85 (1 H, tm, largest coupling 6.5 Hz, 2′- or 3′-H); mass spectrum as for the *erythro*-β-isomer [Found: (e.i.m.s.); M^+, 564.4037. $C_{32}H_{60}O_4Si_2$ requires *M*, 564.4027].

Starting aldehyde (6) (36 mg) was also recovered. The dimer of cyclopentanone was detected by t.l.c., but not isolated.

(*b*) Reactions with the lithium enolate in pentane at −78 °C and in ether at −120 °C were carried out similarly.

(*c*) To a stirred solution of ethyl di-isopropylamine (0.163 g, 1.26 mmol) in pentane (2 ml) at −78 °C was added with care a solution of di-n-butylboron trifluoromethanesulphonate (0.32 g, 1.17 mmol) in pentane (1 ml). Cyclopentanone (91 mg, 1.08 mmol) was added dropwise, and the resulting suspension was stirred at −78 °C for 30 min, allowed to warm to −20 °C during 30 min, and then re-cooled to −78 °C. A solution of the aldehyde (6) (433 mg, 0.902 mmol) in pentane (1 ml) was added dropwise, and the mixture was stirred at −78 °C for 45 min; then as it warmed to 0 °C during 95 min. The reaction mixture was poured into water buffered to pH 7 (phosphate), and worked up *via* extraction and chromatography as described above.

(*d*) To a solution of the lithium enolate of cyclopentanone (0.625 mmol) prepared as described in (*a*), was added at −78 °C triethylboron (M in THF; 0.625 ml). The solution was stirred at −78 °C for 30 min, and a solution of the aldehyde (6) (246 mg, 0.512 mmol) in ether (2.0 ml) was added dropwise. After a further 20 min at −78 °C, aqueous ammonium chloride was added, and the products were isolated as described in (*a*).

A similar experiment was carried out with tri-s-butylboron in place of triethylboron.

(*e*) To a stirred solution of the lithium enolate of cyclopentanone (51 mg, 0.615 mmol), prepared as described in (*a*), but in THF instead of diethyl ether, was added dropwise at −78 °C a solution of dicyclopentadienylzirconium dichloride (181 mg, 0.615 mmol) in THF (3.0 ml). The resulting suspension was stirred for 45 min as it warmed to −50 °C, and was then re-cooled to −78 °C. A solution of the aldehyde (242 mg, 0.504 mmol) in THF (2.0 ml) was added dropwise, and the mixture was stirred at −78 °C for 30 min and then for a further 15 min as it warmed to −50 °C. Methanol (6 ml) and water (6 ml) were added, and the mixture was extracted with ether (4 × 30 ml). The combined extracts were washed with water (2 × 25 ml), and the combined aqueous layers were further extracted with ether (30 ml). The products were isolated from the combined organic layers as described in (*a*).

(*f*) To a stirred solution of the lithium enolate of cyclopentanone (46 mg, 0.555 mmol), prepared as described in (*a*), but in THF, was added dropwise at −78 °C a solution of bromotriphenyltin (0.239 g, 0.555 mmol) in THF (2 ml) and the resulting suspension was stirred at −78 °C for 30 min. A solution of the aldehyde (6) (219 mg, 0.456 mmol) in THF was added in one portion, to give a clear solution, which was stirred at −78 °C for 30 min. Methanol (5 ml) and water (7 ml) were added, and the products were isolated as described in (*e*) and (*a*).

Acknowledgements

We thank the S.E.R.C. for CASE awards (to A. D. B., G. T. W.); Dr. B. E. Mann (University of Sheffield) and Dr. D. Moorcroft (University of Manchester) for high-resolution n.m.r. spectra; Dr. M. D. Lynch for assistance with large-scale syntheses of compound (6); and Dr. F. Scheinmann for useful discussions.

References

1 (*a*) S. M. Ali, M. A. W. Finch, S. M. Roberts, and R. F. Newton, *J. Chem. Soc., Chem. Commun.*, 1979, 679; *ibid.*, 1980, 74; (*b*) S. M. Ali, C. B. Chapleo, M. A. W. Finch, S. M. Roberts, G. T. Woolley, R. J. Cave, and R. F. Newton, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2093.
2 M. A. W. Finch, S. M. Roberts, and R. F. Newton, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1312.
3 C. Gandolfi and G. Doria, *Farmaco, Ed. Sci.*, 1974, **29**, 405.
4 M. A. W. Finch, S. M. Roberts, G. T. Woolley, and R. F. Newton, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1725.
5 R. F. Newton, S. M. Roberts, B. J. Wakefield, and G. T. Woolley, *J. Chem. Soc., Chem. Commun.*, 1981, 922.
6 A. D. Baxter, F. Binns, M. D. Lynch, R. F. Newton, S. M. Roberts, P. Sadler, F. Scheinmann, B. J. Wakefield, and G. T. Woolley, International Conference on Prostaglandins, Florence, 1982; Abstracts p. 131.
7 (*a*) C. H. Heathcock, in ' Comprehensive Carbanion Chemistry,' ed. T. Durst and E. Buncel, Elsevier, Amsterdam, 1982, vol. II; (*b*) C. H. Heathcock, *Science*, 1981, **214**, 395.
8 Y. Yamamoto and K. Maruyama, *J. Am. Chem. Soc.*, 1982, **104**, 2323.
9 D. A. Evans and L. R. McGee, *Tetrahedron Lett.*, 1980, 3975; Y. Yamamoto and K. Maruyama, *Tetrahedron Lett.*, 1980, 4607.
10 Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1981, 162.
11 D. A. Evans, E. Vogel, and J. V. Nelson, *J. Am. Chem. Soc.*, 1979, **101**, 6120; S. Masamune, S. Mori, D. Van Horn, and D. W. Brooks, *Tetrahedron Lett.*, 1978, 1665; but see S. Shenvi and J. K. Stille, *Tetrahedron Lett.*, 1982, **23**, 624.
12 I. G. Vasi and K. R. Desai, *J. Inst. Chem., Calcutta*, 1982, **54**, 19.

Received 18*th January* 1983; *Paper* 3/074