Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 877–881

TETRAHEDRON: *ASYMMETRY*

Rh(II)-binaphthol phosphate catalysts in the enantioselective intramolecular oxonium ylide formation–[3,2] sigmatropic rearrangement of α-diazo-β-ketoesters

David M. Hodgson* and Margarita Petroliagi

Dyson Perrins Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QY, UK

Received 16 February 2001; accepted 22 March 2001

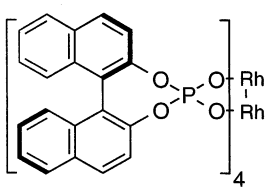
Abstract—The enantioselective intramolecular oxonium ylide formation–[3,2] sigmatropic rearrangement of α-diazo-β-ketoesters **9** using catalytic (1 mol%) dirhodium tetrakisbinaphthol phosphate catalysts **1** and **2** to give benzofuranones **11** in up to 62% e.e. is described.

1. Introduction

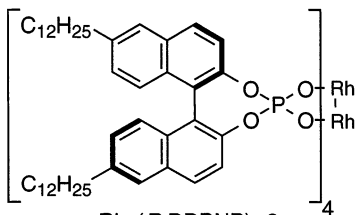
Catalytic enantioselective rearrangements involving ylides from diazo compounds are currently an emerging field in asymmetric synthesis.[1] A variety of chiral non-racemic dirhodium carboxylates and carboxamidates have been extensively examined as asymmetric catalysts in a number of diazocarbonyl transformations.[2] However, our previous investigations revealed that rhodium phosphate catalysts can be superior to these more commonly utilised analogues: we observed enantioselectivities of up to 90% in tandem carbonyl ylide formation–cycloaddition reactions using the binaphthol phosphate (BNP) catalyst $Rh_2[(R)\text{-DDBNP}]_4$ **2**,[3] which at room temperature is a fully hydrocarbon soluble variant of $Rh_2[(R)\text{-BNP}]_4$ **1**.[4] We therefore considered it important to examine the scope of such catalysts in other asymmetric ylide tranformations and present herein the results of our studies on oxonium ylide formation–[3,2] sigmatropic rearrangement.[5]

Seminal studies in 1986 by Pirrung and Werner on the synthesis of furanones by the $Rh_2(OAc)_4$-catalysed [3,2] sigmatropic rearrangement of oxonium ylides from substrates such as α-diazo-β-ketoester **9m** (Scheme 1),[6] and a related report by Johnson and Roskamp,[7] provided the background for the first examples of the corresponding catalytic enantioselective process described in 1992 by McKervey et al.,[8] who used the novel chiral Rh(II) catalyst $[Rh_2(S\text{-BNP})_2(O_2COH)_2{\cdot}5H_2O]$ in refluxing CH_2Cl_2 (the only conditions reported), which gave benzofuranone **10** in 30% e.e. from **8**. Further studies using **9m**[9] led to improved enantiocontrol. After screening a number of Rh(II)-chiral carboxylates as catalysts for the reaction, $Rh_2[(S)\text{-PTTL}]_4$ **3** in hexane was found to give the most selective reaction, affording furanone **11m** with an e.e. of 60%.[10]

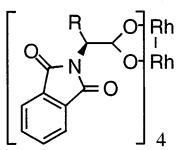
More recently, Clark et al. reported enantioselective intramolecular oxonium ylide formation–[3,2] sigmatropic rearrangements of β′-allyloxy-α-diazoketones using a copper catalyst in combination with a C_2-symmetric diimine which induced e.e.s of up to 57%.[11] Salicyclic acid-derived α-diazoketones gave slightly lower e.e.s (up to 37%). The reaction was discussed as proceeding either by rearrangement via a catalyst-free



$Rh_2(R\text{-BNP})_4$ **1**



$Rh_2(R\text{-DDBNP})_4$ **2**

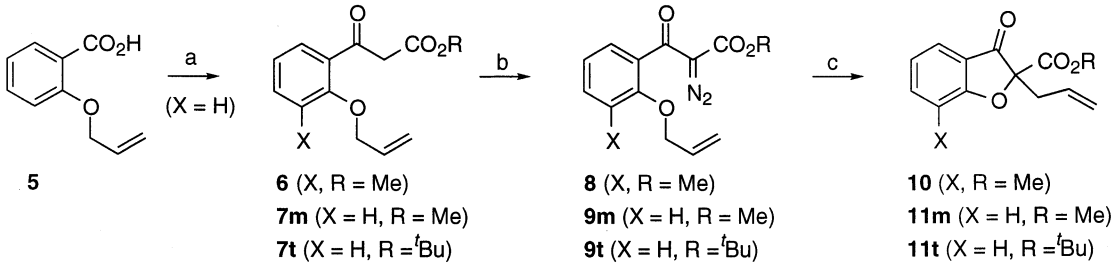


$Rh_2(S\text{-PTTL})_4$ **3** (R = ^{t}Bu)

$Rh_2(S\text{-PTPG})_4$ **4** (R = Bn)

* Corresponding author. E-mail: david.hodgson@chem.ox.ac.uk

0957-4166/01/$ - see front matter
PII: S0957-4166(01)00147-1



5

6 (X, R = Me)
7m (X = H, R = Me)
7t (X = H, R = ^{t}Bu)

8 (X, R = Me)
9m (X = H, R = Me)
9t (X = H, R = ^{t}Bu)

10 (X, R = Me)
11m (X = H, R = Me)
11t (X = H, R = ^{t}Bu)

Scheme 1. (a) Carbonyldiimidazole, THF, 25°C, then $Mg(O_2CCH_2CO_2R)_2$, THF, 25°C, then H_3O^+; (b) 4-(NHAc)$C_6H_4SO_2N_3$, Et_3N, MeCN, 25°C; (c) Rh_2L_4 (cat.), see Table 1.

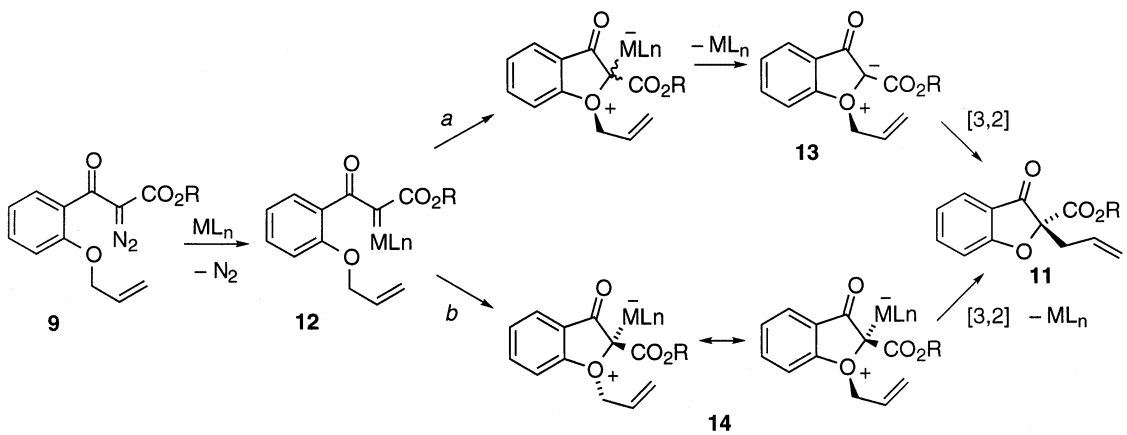
ylide (e.g. **13**, Scheme 2), in which the energy barrier to inversion of configuration at the sp^3 oxonium centre must be significantly greater than the transition state energy for the rearrangement reaction, or an alternative rearrangement through a catalyst bound ylide, such as **14**. If the former process operates (path *a*, Scheme 2), then asymmetric induction is governed by the effectiveness of the ligands on the metal in the putative metallocarbene **12** to discriminate between the (now) diastereotopic lone pairs on the ethereal oxygen. For the latter process (path *b*), ligand-controlled addition to the *Re* or *Si* face of **12** to give **14** is decisive for asymmetric induction, if it is assumed that allylic transposition then occurs exclusively at the rear of the C–ML_n bond in **14** as ML_n dissociates.[1]

In 1998 Doyle et al. reported an enantioselective intramolecular oxonium ylide formation–[3,2] sigmatropic rearrangement to form a ten-membered ring in 65% e.e., and a study of enantioselective *inter*molecular oxonium ylide formation–[3,2] sigmatropic rearrangement, which remarkably occurred in up to 98% e.e. although the reaction yields were poor.[12] Doyle's observation of significant catalyst-dependent diastereoselectivity in this latter work implicates a catalyst-associated ylide in the product-forming step.

2. Results and discussion

Substrates **9** were selected for examination on the basis that they would enable a comparison with the reported studies. Other advantages of studying α-diazo-β-ketoesters (rather than, for example, α-diazoketones) involved their ease of synthesis by diazo transfer, the added ability to vary the ester group and ease of handling of these diazo substrates which are doubly stabilised by the adjacent ester and keto groups. The formation of a quaternary stereocentre in the reaction also precludes the potential for product racemisation.[8] α-Diazo-β-ketoesters **9** were prepared following standard procedures according to Scheme 1. Thus, homologation of the known acid **5**[9] to β-ketoesters **7** was achieved by a modified version of the Masamune procedure,[13] in which the magnesium salts of *mono*-alkyl malonates were prepared using Bu_2Mg rather than $Mg(OEt)_2$.[14] Diazo transfer using 4-acetamidobenzenesulfonyl azide[15] then afforded the rearrangement precursors **9**.

As a starting point for our studies, we attempted to reproduce the best e.e.s reported by McKervey, using α-diazo-β-ketoester **9m**.[10] However, with $Rh_2[(S)$-PTTL$]_4$ **3** (for which the quality was secure—having duplicated enantioselectivities for carbonyl ylide formation–cycloaddition reported[16] by Hashimoto et al.) we obtained product with only 38% e.e. by chiral HPLC (Table 1, entry 2). The original report by McKervey indicated that the e.e. was determined using a chiral shift reagent.[10] However, we were unable to achieve satisfactory resolution with this method of analysis under a variety of concentrations. Baseline resolution was apparently not obtained in the earlier study.[17] We



9 **12** **13** **11** **14**

Scheme 2.

Table 1. Effect of catalyst on the yields and enantioselectivities of formation of benzofuranone **11m** (and **11t**) from α-diazo-β-ketoester **9m** (and **9t**)[a]

Entry	Catalyst	Solvent	T (°C)	Yield of **11** (%)	E.e. of **11** (%)[b]
1	$Rh_2[(S)\text{-PTTL}]_4$	CH_2Cl_2	40	71 (80)	−37[c] (−11)
2	$Rh_2[(S)\text{-PTTL}]_4$	Hexane	25	67 (55)	−38[c] (−17)
3	$Rh_2[(S)\text{-PTTL}]_4$	Hexane	69	69 (66)	−37[c] (−13)
4	$Rh_2[(S)\text{-PTPG}]_4$	Hexane	69	55	−12[c] (−27)
5	$Rh_2[(R)\text{-BNP}]_4$	CH_2Cl_2	25	40 (92)	40 (36)
6	$Rh_2[(R)\text{-BNP}]_4$	CH_2Cl_2	40	54 (56)	37 (15)
7	$Rh_2[(R)\text{-BNP}]_4$	Hexane	25	67 (92)	13 (40)
8	$Rh_2[(R)\text{-BNP}]_4$	Hexane	69	59 (70)	38 (22)
9	$Rh_2[(R)\text{-BNP}]_4$	Benzene	25	48	61
10	$Rh_2[(R)\text{-BNP}]_4$	$C_6H_5CF_3$	25	50	33
11	$Rh_2[(R)\text{-DDBNP}]_4$	CH_2Cl_2	25	66 (80)	41 (41)
12	$Rh_2[(R)\text{-DDBNP}]_4$	CH_2Cl_2	40	33 (95)	48 (36)
13	$Rh_2[(R)\text{-DDBNP}]_4$	Hexane	25	66 (88)	52 (45)
14	$Rh_2[(R)\text{-DDBNP}]_4$	Hexane	69	79 (65)	40 (17)
15	$Rh_2[(R)\text{-DDBNP}]_4$	Benzene	25	46	62
16	$Rh_2[(R)\text{-DDBNP}]_4$	$C_6H_5CF_3$	25	52	31
17	$Rh_2[(R)\text{-DDBNP}]_4$	C_6H_{12}	25	49	48

[a] Yields and e.e.s in parentheses are for *tert*-butyl ester **11t**.

[b] E.e.s were determined by HPLC analysis (see Section 4). A negative value refers to the sign of the specific rotation. Absolute configuration of predominant enantiomer not known.

[c] E.e.s for comparison from Ref. 10 are 47% (entry 1), 60% (entries 2 and 3), 27% (entry 4) and were determined by ^{1}H NMR analysis of the partially[17] split methoxy signal using $Eu(hfc)_3$.

therefore suggest that the method of enantiomer analysis may be the origin of the discrepancy between our results and those of the McKervey group.

Using α-diazo-β-ketoester **9m**, a notable difference in asymmetric induction between $Rh_2[(R)\text{-BNP}]_4$ **1** and $Rh_2[(R)\text{-DDBNP}]_4$ **2** was found in hexane at room temperature, with the benzofuranone **11m** being obtained in 13 and 52% e.e., respectively (entries 7 and 13). E.e.s with the two catalysts converged when reactions were carried out in refluxing hexane (38 and 40% e.e., entries 8 and 14). An explanation for these results may lie in the solubility difference between the catalysts and their associated oxonium ylides: if the catalyst-associated oxonium ylide derived from the hydrocarbon soluble $Rh_2[(R)\text{-DDBNP}]_4$ **2** remained in solution, but the corresponding ylide derived from $Rh_2[(R)\text{-BNP}]_4$ **1** undergoes a more rapid catalyst dissociation (due to its lower solubility in hexane at room temperature) prior to sigmatropic rearrangement, the asymmetric induction with the BNP catalyst would be lower.

There were no other significant differences between carrying out the reaction in chlorinated or hydrocarbon solvents (e.g. entries 11 and 13). Altering the temperature was also found to have little effect on the enantioselectivity of the reaction (e.g. entries 5 and 6; 11 and 12; 13 and 14). Of the hydrocarbon solvents examined, benzene gave the highest enantioselectivities with e.e.s of 61–62% (entries 9 and 15).

Interestingly, when the reaction was conducted in trifluoromethylbenzene, which was used in place of benzene in the same reaction by Hashimoto et al.[16] to minimise metallocarbene insertion into the solvent (presumably due to its comparatively electron deficient aromatic system), significantly reduced e.e.s of benzofuranone **11m** were obtained with both phosphate catalysts (33 and 31%, entries 10 and 16). It should be noted that in Hashimoto's study there was no significant difference in asymmetric induction between these two solvents.[16]

We have previously observed that the size of the ester group exerted a significant effect on e.e. in tandem carbonyl ylide formation–cycloadditions using Rh(II)-BNP-derived catalysts with α-diazo-β-ketoesters (*tert*-butyl esters providing the highest enantioselectivity).[3,18] In the current study with the phosphate catalysts, it was found that although yields generally improved on using *tert*-butyl ester **9t** (Table 1, entries 5–8, 11–13), enantioselectivity was little influenced by the nature of the alkyl substituents. Enantioselectivity increased slightly when using the methyl ester **9m** compared with the *tert*-butyl ester **9t** at room temperature (Table 1, entries 5 and 13); this trend was found to be more pronounced at higher temperatures where e.e.s dropped for the *tert*-butyl ester **9t** under otherwise identical reaction conditions (entries 5 and 6, 11 and 12, and 13 and 14). A notable difference between reactions of the two esters with **1** and **2** is that enantioselectivity is not significantly altered for the reactions of the *tert*-butyl ester **9t** in hexane at room temperature with either catalyst (entries 7 and 13). As discussed earlier there is, however, a marked decrease in the enantioselectivity of the reaction of methyl ester **9m** using the less lipophilic catalyst **1** compared to the equivalent reaction using **2**. This may reflect increased solubility of the catalyst-associated oxonium ylides derived from **9t**, so that solubility effects on asymmetric induction due to the different catalysts are much less pronounced.

3. Conclusions

The present study provides further evidence that the main difference between the catalytic performance of DDBNP and BNP ligands is a result of the solubility in saturated hydrocarbon solvents imparted to $Rh_2[(R)$-DDBNP$]_4$ **2**; there appears to be little, if any, influence on the enantioselectivity of the reaction due to the dodecyl substituents electronically reducing the electrophilic nature of the catalyst, or altering intraplanar (binaphthyl) angles. Whilst there is room for improvement in the levels of asymmetric induction disclosed here, our results show that dirhodium tetrakisbinaphtholphosphate catalysts provide some of the best levels of asymmetric induction in oxonium ylide formation–[3,2] sigmatropic rearrangement reported to date.[1] Further studies on the utility of such catalysts in asymmetric transformations of diazocarbonyl compounds are currently under investigation.

4. Experimental

4.1. General

All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon. Syringes and needles for the transfer of reagents were dried at 140°C and allowed to cool in a desiccator over P_2O_5 before use. Ethers were distilled from sodium benzophenone ketyl; (chlorinated) hydrocarbons and Et_3N from CaH_2. Reactions were monitored by TLC using commercially available glass-backed plates, pre-coated with a 0.25 mm layer of silica containing a fluorescent indicator (Merck). Column chromatography was carried out on Kieselgel 60 (40–63 μm). Light petroleum refers to the fraction with bp 40–60°C. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded as thin films unless stated otherwise. Peak intensities are specified as strong (s), medium (m) or weak (w). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ unless stated otherwise with a Varian Gemini 200 spectrometer. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.26, δ_C (central line of t) 77.0]. Coupling constants (J) are given in Hz. Chiral stationary phase HPLC was performed using a Daicel Chiralpak AD or Chiralcel OJ column (4.6 mm×250 mm) on a Gilson system with 712 Controller Software and a 118 UV–vis detector set at 254 nm. Retention times for major ($t_R$mj) and minor ($t_R$mn) enantiomers are given in min.

4.2. *tert*-Butyl 3-(2-allyloxyphenyl)-3-oxopropionate 7t

1,1′-Carbonyldiimidazole (0.98 g, 6.0 mmol) was added to a stirred solution of 2-allyloxybenzoic acid **5**[9] (0.90 g, 5.1 mmol) in THF (16 cm^3) at 0°C. After stirring the mixture for 10 min the reaction was allowed to warm to room temperature over 1 h. In a separate flask Bu_2Mg (1 M in heptane, 5.6 cm^3, 5.6 mmol) was added dropwise to mono-*tert*-butyl malonate (1.78 g, 11.1 mmol) in THF (16 cm^3) at −78°C and the mixture allowed to stir for 15 min. The reaction was allowed to warm to room temperature over 1 h and evaporated under reduced pressure. The imidazolide solution was added via cannula to the magnesium salt and the resulting reaction mixture stirred overnight at room temperature. After evaporation under reduced pressure, the reaction mixture was dissolved in Et_2O and washed with 10% citric acid, saturated aq. $NaHCO_3$, dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (3/1, Et_2O/light petroleum) followed by distillation (bp 100°C/0.5 mbar) gave a yellow oil of β-ketoester **7t** (0.50 g, 36%); IR: 2980m, 1733s, 1674s and 1598s cm^{-1}; ^{1}H NMR: δ 1.41 (9H, s, ^{t}Bu), 3.94 (2H, s, CH_2CO), 4.65 (2H, dt, J 5.5 and 1.5, OCH_2), 5.35–5.46 (2H, m, $=CH_2$), 5.95–6.21 (1H, m, CH=CH$_2$), 6.93–6.99 (2H, m, ArCH), 7.45–7.55 (1H, m, ArCH) and 7.81–7.85 (1H, m, ArCH); ^{13}C NMR: δ 28.3 (CMe_3), 52.2 (CH_2CO_2), 69.9 (OCH_2CH), 81.6 (CMe$_3$), 113.1 (Ar), 118.9 (=CH$_2$), 121.3 (Ar), 127.4 (Ar, quat.), 131.3 (Ar), 132.9 (Ar), 134.7 (CH=CH$_2$), 158.4 (Ar, quat.), 167.7 (CO_2) and 194.3 (COCH$_2$); MS (CI-NH$_3$): m/z 277 (M+H$^+$, 23%), 238 (100), 221 (25) and 177 (82) (found: M+H$^+$, 277.1447. $C_{16}H_{21}O_4$ requires: M, 277.1440).

4.3. *tert*-Butyl-2-diazo-3-(2-allyloxyphenyl)-3-oxopropionate 9t

Et_3N (0.40 cm^3, 2.9 mmol) was added dropwise to a stirred solution of β-ketoester **7t** (379 mg, 1.37 mmol) and 4-acetamidobenzenesulfonyl azide (390 mg, 1.62 mmol) in MeCN (6 cm^3) at 0°C and then the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was evaporated under reduced pressure to give a residue which was dissolved in Et_2O. Light petroleum was added to the solution, followed by filtration (to remove sulfonamide) and evaporation under reduced pressure to give a residue which was purified by column chromatography (2/1, EtOAc/light petroleum) to give a yellow oil of α-diazo-β-ketoester **9t** (265 mg, 64%); IR: 2979m, 2140s, 1723s, 1692m, 1627m and 1599m cm^{-1}; ^{1}H NMR: δ 1.44 (9H, s, Bu^t), 4.59–4.64 (2H, m, OCH_2), 5.30–5.52 (2H, m, $=CH_2$), 5.99–6.19 (1H, m, CH=CH$_2$), 6.97–7.07 (2H, m, ArCH) and 7.30–7.52 (2H, m, ArCH); ^{13}C NMR: δ 27.8 (CMe_3), 68.9 (OCH_2), 82.7 (CMe$_3$), 111.9 (Ar), 117.2 (=CH$_2$), 120.8 (Ar), 128.6 (Ar), 128.8 (Ar, quat.), 132.3 (Ar), 132.8 (CH=CH$_2$), 156.0 (Ar, quat.), 160.2 (CO_2) and 186.9 (CO); MS (CI-NH$_3$): m/z 303 (M+H$^+$, 16%), 264 (32), 247 (23), 238 (35), 236 (28) and 177 (100) (found: M+H$^+$, 303.1346. $C_{16}H_{19}N_2O_4$ requires: M, 303.1345).

4.4. Benzofuranone formation: general procedure

The rhodium catalyst (1 mol%) and α-diazo-β-ketoester **9** (0.01 M in degassed[19] solvent) were stirred at the temperature indicated in Table 1. After completion of the reaction as judged by TLC (3–36 h for reactions at 25°C; ca. 3 h for reactions at reflux), the reaction mixture was evaporated under reduced pressure and the residue purified by column chromatography.

4.4.1. 2-Allyl-2-methoxycarbonyl-2,3-dihydrobenzofuran-3-one 11m[9]. E.e.s were determined by HPLC (Daicel Chiralpak AD, 1% EtOH/hexane, 0.45 cm^3 min^{-1}); $t_R$mn (for (*R*)-phosphate catalysts), 16.9; $t_R$mj (for (*R*)-phosphate catalysts), 10.6.

4.4.2. 2-Allyl-2-*t*-butoxycarbonyl-2,3-dihydrobenzofuran-3-one 11t. ^{1}H NMR: δ 1.51 (9H, s, ^{t}Bu), 2.85 (1H, dd, *J* 7 and 14.5, H of CH_2), 3.10 (1H, dd, *J* 7 and 14.5, H of CH_2), 5.10–5.40 (2H, m, $=CH_2$), 5.65–5.90 (1H, m, CH=), 7.18–7.34 (2H, m, ArCH) and 7.70–7.72 (2H, m, ArCH); ^{13}C NMR: δ 28.2 (CMe_3), 38.5 ($CH_2CH=$), 84.2 (CMe_3), 91.7 ($COCCO_2$), 113.9 (Ar), 119.0 (Ar, quat.), 120.8 ($=CH_2$), 122.9 (Ar), 125.3 (Ar), 130.4 (Ar), 138.9 ($CH=CH_2$), 165.0 (Ar, quat.), 172.8 (CO_2) and 195.0 (CO); MS (CI-NH_3): *m*/*z* 292 ($M+NH_4^+$, 100%), 236 (95) and 192 (50) (found: $M+NH_4^+$, 292.1549. $C_{16}H_{22}NO_4$ requires: *M*, 292.1549). E.e.s were determined by HPLC (Daicel Chiralcel OJ, 2% EtOH/hexane, 0.45 cm^3 min^{-1}); $t_R$mn (for (*R*)-phosphate catalysts), 14.1; $t_R$mj (for (*R*)-phosphate catalysts), 16.5.

Acknowledgements

This work was supported by a Marie Curie Fellowship of the European Community (programme TMR under contract number HPMF-CT-1999-00273). We also thank the EPSRC National Mass Spectrometry Service Centre for mass spectra.

References

1. Hodgson, D. M.; Pierard, F. Y. T. M.; Stupple, P. A. *Chem. Soc. Rev.* **2001**, *30*, 50–61.
2. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley-Interscience: New York, 1998.
3. Hodgson, D. M.; Stupple, P. A.; Johnstone, C. *Chem. Commun.* **1999**, 2185–2186.
4. Pirrung, M. C.; Zhang, J. *Tetrahedron Lett.* **1992**, *33*, 5987–5990.
5. Markó, I. E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds. The Stevens and related rearrangements. Pergamon Press: Oxford, 1991; Vol. 3, pp. 913–974.
6. Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060–6062.
7. Roskamp, E. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 6062–6063.
8. McCarthy, N.; McKervey, M. A.; Ye, T.; McCann, M.; Murphy, E.; Doyle, M. P. *Tetrahedron Lett.* **1992**, *33*, 5983–5986.
9. Ye, T.; Fernández García, C.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1373–1379.
10. Pierson, N.; Fernández-García, C.; McKervey, M. A. *Tetrahedron Lett.* **1997**, *38*, 4705–4708.
11. Clark, J. S.; Fretwell, M.; Whitlock, G. A.; Burns, C. J.; Fox, D. N. A. *Tetrahedron Lett.* **1998**, *39*, 97–100.
12. Doyle, M. P.; Forbes, D. C.; Vasbinder, M. M.; Peterson, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 7653–7654.
13. Brooks, D. W.; Lu, L. D.-L.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 72–74.
14. Ghosh, M.; Miller, M. J. *Tetrahedron* **1996**, *52*, 4225–4238.
15. Baum, J. S.; Shook, D. A.; Davies, H. M. L.; Smith, H. D. *Synth. Commun.* **1987**, *17*, 1709–1716.
16. Kitagaki, S.; Masahiro, A.; Kataoka, O.; Matsuno, K.; Umeda, C.; Watanabe, N.; Hashimoto, S. *J. Am. Chem. Soc.* **1999**, *121*, 1417–1418.
17. Pierson, N. Ph.D. Thesis, The Queen's University, 1997, Fig. 2.13b.
18. Stupple, P. A. D.Phil. Thesis, University of Oxford, 1999.
19. Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063–3070.