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^tBuMe₂, Et₃)

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ASYMMETRIC SILVLPHOSPHITE ESTERS: SYNTHESIS AND REACTIVITY OF (*rac-0,0-B*INAPHTHOLATO)POSiR₃ ($R_3 = Ph_3$, ^tBuMe₂, Et₃)

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Abstract: The new, silvlphosphite compounds, $(rac-O, O-binaphtholato)POSiR_3$ (R₃ = Ph₃, ^tBuMe₂, Et₃) have been synthesised by the reactions of (rac-O, O-binaphtholato)PCl and R₃SiOH. The abilities of these silvlphosphite esters to act as phosphonylating agents towards benzaldehyde have been investigated.

We are currently investigating the use of chiral silylated organophosphorus(III) reagents of the form (XY)POSiR₃ (where XY is a di-anionic chelating chiral auxiliary and $R_3 = Me_3$, Ph₃, ^tBuMe₂, Et₃) in the asymmetric phosphonylation of prochiral unsaturated organic substrates such as aldehydes.¹ One of our aims is to develop an asymmetric variant of the Abramov reaction² (Scheme 1).

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To this end we recently reported asymmetric phosphonylations using reagents containing phosphorus-coordinated (1R,2S)-ephedrine auxiliaries.¹ One of the major disadvantages of this system is that reaction with a prochiral substrate such as benzaldehyde, in an Abramov-type reaction, leads to four possible stereoisomeric products. Theoretically, the situation can be simplified by using an auxiliary that possesses C_2 symmetry where only a single stereoisomeric form exists for the silylated organophosphorus(III) reagent and hence only two possible isomers can be produced in the reaction with benzaldehyde. We have recently reported the synthesis of silylphosphites containing chiral (+)-dimethyl-L-tartrate esters as auxiliaries but these compounds do not react very cleanly with benzaldehyde.³ Consequently, it is desirable to have more robust systems containing C_2 symmetric auxiliaries and here we wish to report studies using binaphthol, an auxiliary that has been shown to possess excellent chiral recognition properties in other systems.⁴

(rac-O, O-binaphtholato)PCl 1 was islolated in high yield from the reaction in Scheme 2. This compound has been prepared previously by Pringle and coworkers.⁴ Two potential routes exist from 1 to our target compounds of the form (rac-O, O-binaphtholato)POSiR₃ but we have found that only one of these allows access to the silylphosphite esters cleanly and in high yield. Stoichiometric hydrolysis of 1 affords (rac-O, O-binaphtholato)P(=O)H 2 cleanly but subsequent silylation of 2 with Me₃SiCl and NEt₃ does not proceed cleanly, unlike analogous





reactions of other secondary phosphites.⁵ Three ³¹P NMR resonances are observed in the region expected for (*rac-O,O*-binaphtholato)POSiMe₃ at δ 139.4, 137.0 and 136.2 ppm but a significant amount of the product mixture is (*rac-O,O*-binaphtholato)PCl 1 (δ 178.6). One possible rationale for the formation of 1 in this reaction is illustrated in equations 1 and 2 below.

NEt₃ (binaphtholato)P(=O)H + Me₃SiCl \longrightarrow (binaphtholato)POSiMe₃ + NHEt₃Cl (1) (binaphtholato)POSiMe₃ + Me₃SiCl \longrightarrow (binaphtholato)PCl + (Me₃Si)₂O (2)

However, 1 can be silvlated directly by reaction with a stoichiometric quantity of R_3SiOH and NEt_3 , resulting in isolation of the silvlphosphite esters, (*rac-O,O*-binaphtholato)POSiR₃ ($R_3 = Ph_3$ 3, ^tBuMe₂ 4, Et₃ 5) as white crystalline solids in high yield. Although we have not yet been able to grow crystals suitable for X-ray analysis, mass spectral and molecular weight studies suggest that

3-5 are monomeric. Specifically, no peaks higher than those of the monomeric molecular ion were observed in the mass spectra of 3-5 (*m/e* 590, 446 and 446 respectively) and molecular weight measurements on 3 and 4 were consistent with monomeric species; found for 3, 583 (required 591) and found for 4, 455 (required 447).

The silylphosphite esters 3-5 do not react with benzaldehyde at room temperature in toluene solvent, a result similar to that obtained with (*O*,*O*dimethyltartrato)POSiR₃.³ However, warming a stoichiometric mixture of 3, 4 or 5 with benzaldehyde to 80°C in toluene solvent does lead to reaction. By ³¹P NMR spectroscopy, resonances at δ 31.9 and 31.4, δ 31.5 and 31.1 and δ 31.9 and 31.4 may be assigned to the two possible diastereoisomers of the α -siloxo phosphonate esters 6, 7 and 8 respectively (Scheme 2). The reactions appear to be cleaner than those involving (*O*,*O*-dimethyltartrato)POSiR₃ but are still very slow; with 6, 7 and 8 accounting for only 11%, 16% and 12% respectively of the product mixtures after 72 h at 80°C in toluene.

We are currently examining ways of increasing the reactivity of phosphorus(III) esters towards aldehydes and to devise asymmetric variants thereof.⁶

Experimental

All manipulations were carried out under an atmosphere of dry dinitrogen gas using Schlenk and cannula techniques or in a dinitrogen-filled dry box. Solvents were pre-dried over either sodium wire, calcium chloride or 4 A molecular sieves before reflux and subsequent distillation, under dinitrogen, from a suitable drying agent (given in parentheses); pentane (sodium benzophenone ketyl) and toluene (sodium metal). All solvents were freshly deoxygenated before use. IR spectra were recorded on Perkin-Elmer 257 and 457 grating spectrophotometers as nujol mulls (cm⁻¹). Mass spectra were obtained on a VG Autospec instrument in the electron impact mode. NMR spectra were obtained on JEOL FX 90Q, JEOL FX 100 or Bruker AM 400 instruments. Deuterated solvents were dried by passage down a column of basic alumina (Brockmann Grade I) and deoxygenated before use. All spectra are reported at 298 K in CDCl₃ unless stated otherwise. Molecular weight measurements were made on an Hitachi Perkin-Elmer 115 Molecular Weight Apparatus. Elemental analyses were performed by the Microanalytical Laboratory of this Department. The compounds *rac*-binaphthol, PCl₃, NEt₃ and R₃SiOH were purchased from commercial sources and were either recrystallised (Ph₃SiOH), chromatographed on a short column of Brockmann Grade I basic alumina (NEt₃, ^tBuMe₂SiOH, Et₃SiOH) or used as received (PCl₃, *rac*-binaphthol).

Synthesis of (rac-O,O-binaphtholato)PCl 1

A suspension of 1,1'-*rac*-binaphthol (2.59 g, 9.06 mmol) in toluene solvent (50 cm³) was added dropwise to a solution of PCl₃ (0.79 cm³, 9.06 mmol) and NEt₃ (2.52 cm³, 18.1 mmol) at -78°C. The initially pale yellow solution turned green over a period of a few hours and precipitation of NHEt₃Cl occurred. After stirring overnight, the mixture was filtered, the residue washed with toluene (2 x 5 cm³) and the volatiles removed from the combined extracts under reduced pressure to afford pale coloured crystals of 1. Yield, 2.77 g (87%). $\delta_{\rm P}$ 178.8 (s).

Synthesis of (rac-O,O-binaphtholato)P(=O)H 2

A suspension of 1,1'-*nac*-binaphthol (2.59 g, 9.06 mmol) in toluene solvent (50 cm³) was added dropwise to a solution of PCl₃ (0.79 cm³, 9.06 mmol) and NEt₃ (2.52 cm³, 18.1 mmol) at -78°C. The initially pale yellow solution turned

green over a period of a few hours and precipitation of NHEt₃Cl occurred. After stirring overnight, the mixture was filtered, the residue washed with toluene (2 x 5 cm³) and all extracts combined. The filtrate was treated with H₂O (0.16 cm³, 9.06 mmol) and NEt₃ (1.26 cm³, 9.06 mmol) at room temperature whereupon the initially clear, green solution turned cloudy rapidly as NHEt₃Cl precipitated. After stirring for 1 h, the solution was filtered and the volatiles removed under reduced pressure. The resulting white solid was washed with pentane (2 x 10 cm³) and dried *in vacuo*. Yield, 2.2 g (73%). IR, 1197 {s br, v(P=O)}; $\delta_{\rm H}$ 8.29-7.36 (m, 12H, Ph-H), 7.50 (s, 1H, ¹J_{PH} 724, P-H); $\delta_{\rm P}$ 14.0 (s); *m/e*, 331 (M)⁺.

Syntheses of $(rac-0, 0-binaphtholato)POSiR_3$ $(R_3 = Ph_3 3, tBuMe_2 4, Et_3 5)$

A solution of Ph₃SiOH (0.4 g, 1.44 mmol) was added dropwise at room temperature to a stirred solution of 1 in toluene (0.5 g, 1.44 mmol in 15 cm³). The mixture was stirred thus for 16 h after which time it was filtered, the residue washed with toluene (2 x 5 cm³), all extracts combined and the volatiles removed under reduced pressure. The resulting white solid was washed with pentane (2 x 10 cm³) and dried *in vacuo*. Yield of 3, 0.71 g (83%); Found, C 77.25%, H 4.75%, Calc. for C₃₈H₂₇O₃PSi, C 77.27%, H 4.61%; IR, 936 {s, br, v(POSi)}; $\delta_{\rm P}$ 138.1 (s); *m/e*, 590 (M)⁺, 513 (M - Ph)⁺, 332 (M - Ph₃Si)⁺.

Compounds 4 and 5 were prepared using an analogous procedure.

For 4: Yield 63%; Found, C 69.75%, H 6.05%, Calc. for $C_{26}H_{27}O_3PSi$, C 69.93%, H 6.10%; IR, 939 {s,br, v(POSi)}; δ_H 8.19-7.37 (m, 12H, Ph-*H*), 1.12 (s, 9H, ^tBu), 0.30 (s, 3H, SiMe₂), 0.21 (s, 3H, SiMe₂); δ_P 139.4 (s); *m/e*, 446 (M)⁺. For 5: Yield 79%; IR, 940 {s,br, v(POSi)}; δ_H 7.76-7.02 (m, 12H, Ph-*H*), 0.76 (t, 9H, ³J_{HH} 8, CH₃CH₂), 0.46 (q, 6H, ³J_{HH} 8, CH₃CH₂); δ_P 139.1 (s); *m/e*, 446 (M)⁺, 417 (M - Et)⁺, 389 (M - Et₂)⁺, 332 (M - Et₃Si)⁺.

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