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A structural and mechanistic investigation of the mono-*O*-phenylation of diols with $BiPh_3(OAc)_2$

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Abstract

The mono-*O*-phenylation of enantiomerically pure pinanediol **2** using $BiPh_3(OAc)_2$ **1** and the biphenyl-2,2′-ylenephenylbismuth analogue **9** has been investigated. It is postulated that reductive elimination at the trigonal bipyramidal bismuth (V) centre of **1** upon exposure to ambient light affects the transfer of an apical phenyl ligand to the least sterically encumbered hydroxyl group of the diol, affording the monophenyl ether in good yield. $SbPh_3(OAc)_2$ fails to undergo reductive elimination, affording the stable diolate **6** instead. The X-ray crystal structure of **6** provides a reasonable model for the intermediate of the bismuth mono-*O*-phenylation, and suggests further studies with bismuth complexes such as **9** possessing intramolecularly tethered ligands incapable of facilitating the mono-*O*-phenylation reaction. The discussions are supported by X-ray crystallographic correlations, and calculations indicate that (M)-(−)-**6** adopts the lowest energy conformational diastereoisomer.

Keywords: Mono-*O*-phenylation; Organobismuth; Propellers

1. Introduction

The photoredox processes associated with main group metal complexes are relatively rare and as such remain a neglected area of study. They are invariably initiated by metal-centred or charge-transfer excited states which lead to inter- and intramolecular reactions [1]. David and Thieffry reported that refluxing CH_2Cl_2 (DCM) solutions of 1,*n*-diols ($n = 2–6$) are selectively mono-*O*-phenylated with $BiPh_3(OAc)_2$ (**1**) in good to excellent yields [2]. *O*-Phenylation was invariably accompanied by an induction period of up to 2 h, and in addition to being solvent selective, photochemical activation was required [3]. Although the rate of mono-*O*-phenylation is found to decrease with increasing chain length ($n = 2 \rightarrow 6$), overall yields remained high. Excellent regioselectivity was observed in the case of secondary versus tertiary hydroxyl groups. The process of *O*-phenylation was found to require the *participation* of an ancillary functionality such as an alkyl/aryl ether [4]. These observations led David and Thieffry to propose that *O*-phenylation is attended by a cyclic transition structure reminiscent of **7** (Fig. 1) [5], in which a trigonal bipyramidal (TBPY) Bi(V) centre accommodates a diolate species at the equatorial and axial coordination sites; the least encumbered acceptor functionality occupying the sterically undemanding equatorial co-ordination site. It was presumed that the relief of steric pressure drives the transfer of the axial phenyl ligand to the equatorial acceptor functionality. In an attempt to probe the synthetic utility of the mono-*O*-phenylation reaction, and to investigate the model proposed by David and Thieffry, we present herein a mechanistic and structural study as a contribution towards the understanding of photoredox processes of main group elements. We have recently demonstrated that inversion of the propeller configuration [6] of co-ordinated PPh_3 is a major contributor to the switch of specific rotation in chiral metal complexes [7]. We now report the first example of a stereogenic XPh_3 propeller unit incorporated within an enantiomerically pure TBPY dioxo

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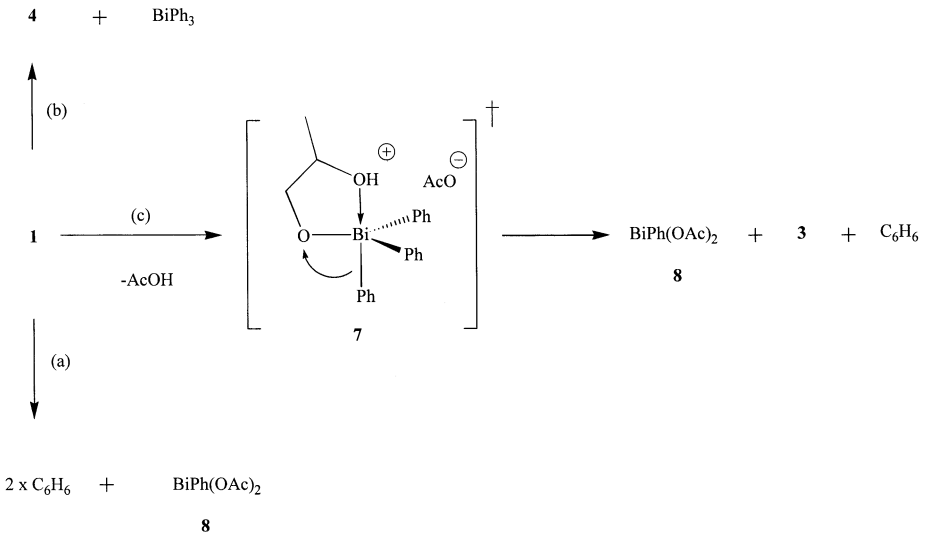


Fig. 1. Conditions, (a) DCM-d_2, ambient light or 366 nm; (b) **2**, DCM-d_2, Δ; (c) **2**, DCM-d_2, ambient light, Δ.

chelate, and comment upon the implications for the stereoisomerisation processes within such systems.

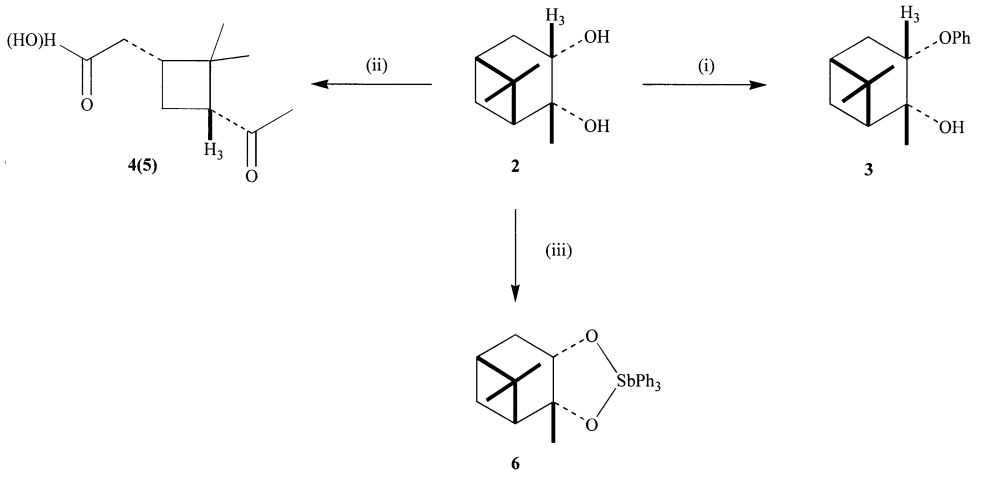
2. Results

(−)-Pinanediol **2**[1] was chosen as the model substrate for our studies as it possesses vicinal secondary/tertiary hydroxyl groups; a combination expected to afford complete regioselectivity (i.e. **2**→**3**, Scheme 1). It is cheap and readily available in both enantiomeric forms and is therefore potentially amenable to stereochemical investigations if necessary. The diol **2** and the (C-3)-*O*-phenyl ether **3** may be readily distinguished from each other in the crude reaction mixture by the ^{1}H-NMR resonance associated with the hydrogen atom geminal to the acceptor (secondary) hydroxyl moiety [i.e. H-3 δ ($CDCl_3$) = 3.94 (**2**) and 4.54 (**3**) ppm]. Furthermore, the ^{1}H-NMR spectrum of commercially available *cis*-pinonic acid[2] **5** (δH-3 = 2.87 ppm), allows ready identification of aldehyde **4**, the product of glycol cleavage [8].

In a typical procedure, equimolar quantities of **1** and (−)-**2** were refluxed in DCM for 2 h, affording **3** (79%) and **4** (13%) and unreacted (−)-**2** (8%). Under particularly bright ambient conditions, synthetically useful yields of **3** (66%) were produced after only 10 min, accompanied by small amounts of **4** (8%) and unreacted starting material (−)-**2** (26%). However, low natural light levels afforded yields of **3** in the range 2–8% even after 5 h, with glycol cleavage being the significant process (36–49%). The participation of photo-generated aryl radical species was readily investigated by the addition of one and two equivalents of 1,1-diphenylethylene, an efficient radical scavenger [9], to solutions of **2** and **1** in refluxing DCM. After 4 h in strong sunlight, ^{1}H-NMR analyses of the crude mixtures revealed the yield of **3** (ca. 70%) to be similar to that of a control reaction. It was concluded therefore that photo-generated aryl radical species do not play a significant role in mono-*O*-phenylation.

NMR studies were carried out to examine the fate of **1** during the course of *O*-phenylation. A DCM-d_2 solution of **1** was irradiated for 1 h at 366 nm, producing a fine white precipitate. NMR analysis revealed the appearance of additional resonances at δ = 8.45 (d), 7.88 (t) δ = 7.35 (s) and 1.92 (s) ppm. The low field singlet was attributed to C_6H_6. The remaining resonances are attributed to $BiPh(OAc)_2$ **8**, which ultimately polymerises to afford an insoluble precipitate (Fig. 1a) [10]. An equimolar quantity of **1** was added to a DCM-d_2 solution of (−)-**2**, and the mixture was monitored via ^{1}H-NMR at room temperature in the absence of light for 12 h. *O*-Phenylation was not observed. The product of glycol cleavage **4** was however noted almost immediately, accompanied by the formation of $BiPh_3$ (Fig. 1b). Irradiation (366 nm) of the crude reaction mixture after 12 h afforded the mono-*O*-phenylated material **3** (22%). The crude reaction mixture attending the mono-*O*-phenylation of **2** with **1** in DCM-d_2 contains—in varying degrees depending upon the reaction conditions—**3**, **8**, **4**, C_6H_6 and $BiPh_3$, in addition to a fine white precipitate (Fig. 1c). In the absence of strong light, oxidation of the substrate predominates with the concomitant formation of $BiPh_3$. The formation of $BiPh(OAc)_2$ **8** would appear to accompany both the light

[1] [1*R*-(1α,2α,3α,5α)]-2,6,6-Trimethylbicyclo[3.1.1]heptane-2,3-diol.
[2] *cis*-3-Acetyl-2,2-dimethylcyclobutaneacetic acid.



Scheme 1. Reagents: (i) **1**, Δ, light, DCM; (ii) **1**, Δ, DCM, and (iii) $SbPh_3(OAc)_2$, TMG, DCM.

induced decomposition of **1**, and the mono-*O*-phenylation of **2**.

A DCM-d_2 solution of (−)-**2** was treated with one equivalent of $SbPh_3(OAc)_2$ under varying levels of natural light and refluxed for 4 h. Neither substrate oxidation nor mono-*O*-phenylation were observed via ^{1}H-NMR spectroscopy. However, an alternative product, characterised as **6** [11] (Scheme 1) was detected upon initial mixing, the concentration of which remained unchanged after 4 h reflux (40%). The addition of TMG increased the concentration of **6** to 87%. This represents the most expeditious route to **6** reported to date. Irradiation of the crude reaction mixture (366 and 254 nm) failed to initiate mono-*O*-phenylation. Single crystals of **6** were grown from a dichloromethane solution layered with hexane. The molecular structure of **6** is presented in Fig. 2 together with the atomic numbering scheme, whilst selected bond lengths and angles are presented in Table 1. The complex possesses a distorted TBPY molecular geometry about the metal centre, where O(1) of the diolate and C(23) occupy the axial and O(2)/C(11)/C(17) occupy the equatorial coordination sites.

Like **1**, phenylbiphenyl-2,2′-ylenebismuth diacetate **9** (Fig. 3) reacts with a variety of nucleophiles to afford good yields of *C*-phenylated substrates [12]. Equimolar quantities of **9** and (−)-**2** were refluxed in DCM in strong ambient light. After three attempts, only trace amounts of the *O*-phenyl ether **3** could be observed after 4 h reflux. On each occasion, the product was **4**, that of glycol cleavage (60%, 0.6 h). In our hands, both *cis*- and *trans*-cyclohexane-1,2-diols are smoothly transformed to the corresponding *O*-phenyl ethers using **1** in excellent yields (> 90%). The analogous bismuth complex **9** fails to affect the corresponding transformation after 4 h reflux.

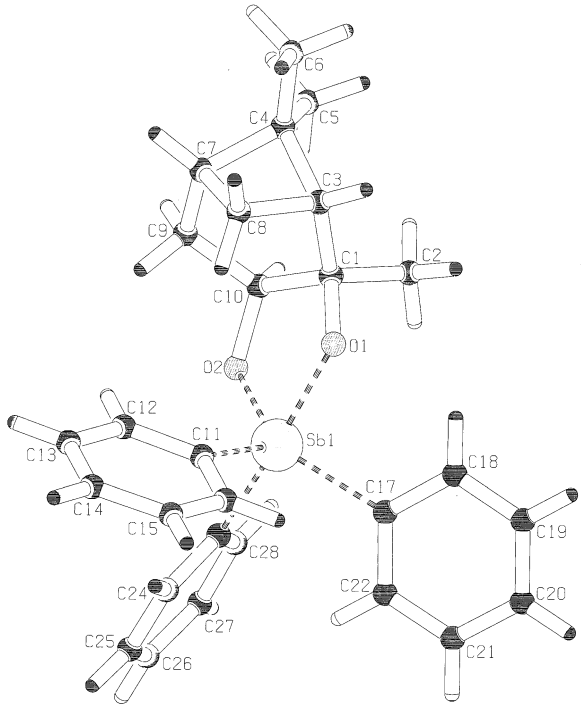


Fig. 2. The X-ray crystal structure of (−)-(M)-**6**.

3. Discussion

In an analogous fashion to the transition metals, main group elements have been classified according to the electronic configuration of the ground state. Thus, Bi(V) and Sb(V) complexes possessing empty valence shells (i.e. ns^0np^0) are classified as s^0. Consequently, the only electronic transitions available to s^0 complexes are the ligand to metal charge transfer (LMCT) type. Although few examples have been reported [13], reductive elimination appears to be the characteristic photoreaction of

Table 1
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths	
C11–Sb	12.118(3)
C17–Sb1	2.143(3)
C23–Sb1	2.161(3)
O1–Sb1	2.008(2)
O2–Sb1	1.989(2)
Bond angles	
O2–Sb1–O1	80.11(9)
O2–Sb1–C11	113.09(11)
O2–Sb1–C17	136.78(10)
O2–Sb1–C23	84.86(10)
O1–Sb1–C23	162.81(11)

s^0 metal complexes. Our interest in $SbPh_3(OAc)_2$ as a potential reagent for mono-*O*-phenylation was stimulated by the observation that electronic excitation of the s^0 complex $[Sb(V)Cl_6]^-$ [14] is attended by an efficient two electron reduction of the metal affording Cl_2. However unlike **1**, $SbPh_3(OAc)_2$ forms the stable diolate complex **6** which fails to undergo reductive elimination even when irradiated. In contrast with the d^0 configuration of transition metals, the oxidation strength of s^0 complexes decreases down the group, as does the energy of the LMCT transitions. The variation in photoreactivity between the antimony and bismuth complexes is therefore a reflection of the relative energies of LMCT transitions.

Further analysis of the X-ray crystal structure of antimony complex **6** is warranted for two reasons, namely; (i) it constitutes the first example of a stereogenic XPh_3 moiety incorporated within an enantiomerically pure bidentate dioxo-ligand, and (ii) it is a reasonable model for **7**, the proposed transition-state for the mono-*O*-phenylation of **2** with **1** (Fig. 1).

A search of the Cambridge structural database (CSD refcodes supplied in reference section) for five co-ordinate systems analogous to **6**, possessing an integral triphenyl unit XPh_3 (X = central atom) and a five-membered dioxo-chelating ligand reveals examples of both SP and TBPY arrangements (Fig. 3). Dioxo chelates within distorted [15] SP structures (X = P [16], Sb [17], Sn [18]) invariably span the basal edge, whereas the corresponding chelate within TBPY systems occupy the axial (O^{ax}) and equatorial (O^{eq}) sites [19]. This and previous studies [20] clearly demonstrate that the more crowded oxygen atom of a non-symmetrical dioxo chelate occupies the least crowded axial co-ordination site (O^{ax}) of a TBPY arrangement. The observed regioselectivity of mono-*O*-phenylation is therefore conveniently accounted for by invoking a transition state resembling a TBPY arrangement such as **7**.

When two or more aryl rings are bonded to a central atom X (i.e. the $SbPh_3$ unit of **6** for example) rotation about a given X–C_i bond is coupled in the sense that no ring moves independently of the other two [21]. Aryl rings within such systems afford a correlated arrangement which may be described in terms of two enantiomeric propeller configurations, i.e. *clockwise* (P) and *anti-clockwise* (M), respectively [22]. These conformational alternatives are illustrated for the proposed reactive intermediate **7** (Newman projections, Fig. 4). A high energy achiral arrangement—which resembles the transition-state for the one ring-flip stereoisomerisation process—is also observed in the solid state [19]. Assuming that the conformations adopted in the solid-state represent favoured arrangements on the potential energy surface of a complex, the observation of achiral and chiral arrangements indicate a low energy stereoisomerisation pathway for P↔M via the achiral structure. The X-ray crystal structure of (−)-**6** adopts the (M) propeller configuration, and therefore constitutes a favoured arrangement on the potential energy surface of the stereoisomerisation pathway P↔M. When the metal centre is co-ordinated to an achiral dioxo-chelate, the propeller conformers are degenerate and as such are expected to occur randomly. However, as in the case of **6** where the dioxo-chelate is chiral, the propeller conformers are rendered diastereoisomeric and as such are not expected to occur in equal amounts. The X-ray crystal structure of (M)-(−)-**6**, which constitutes the first example of a XPh_3 moiety incorporated within an enantiomerically pure bidentate ligand, is expected to be lower in energy than the corresponding conformational diastereoisomer (P)-(−)-**6**. Single point energy calcula-

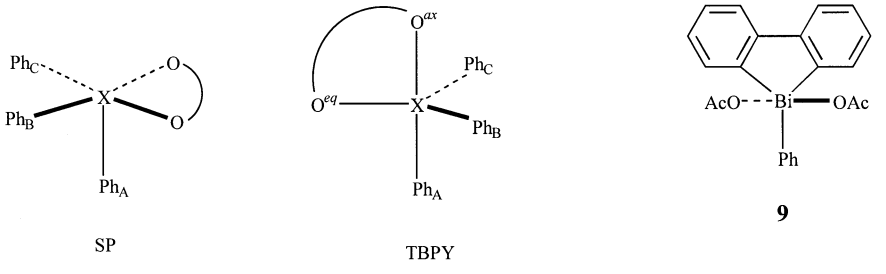


Fig. 3. Structural alternatives for a penta co-ordinate metal possessing an integral triaryl unit and a five-membered dioxo-chelate.

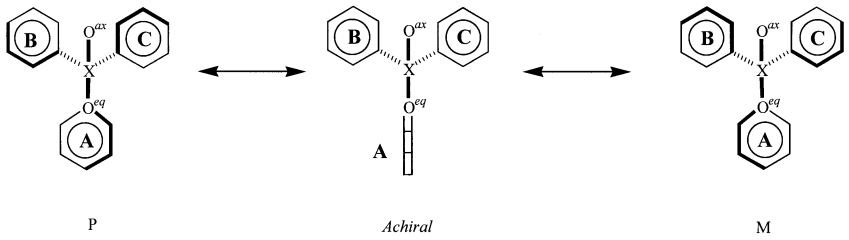


Fig. 4. The low energy stereoisomerisation pathway for (P)↔(M) via the higher energy achiral arrangement.

tions[3] upon the optimised structure (M)-(−)-**6**, and the corresponding conformational diastereoisomer (P)-(−)-**6** indicate a significant preference for the former ($\Delta E =$ 30 kJ mol^{-1}).[4] This preference may be readily appreciated by considering Newman projections of the conformational diastereoisomers (M)-(−)-, and (P)-(−)-**6** (Fig. 5). Complex **6** adopts the (M)-(−)-conformational diastereoisomer in the solid-state, thereby orienting the bridgehead methyl moiety (C10) of the pinane fragment above the face of phenyl ring B. The epimeric conformational diastereoisomer (P)-(−)- orients the corresponding methyl moiety (C10) above the sterically demanding *edge* of phenyl ring B, thereby generating a clashing interaction.

In accord with the model of David and Thieffry, the X-ray crystal structure of **6** strongly suggests that the axial phenyl ligand Ph_A of the TBPY arrangement couples with the neighbouring acceptor functionality of the co-ordinated diol (i.e. $Ph_A \rightarrow O^{eq}$, Fig. 3). This possibility is supported by the fact that Ph_A possesses the weakest M–C_i bond [i.e. Sb–Ph_A (C23) = 2.16 Å; Sb–Ph_B (C11) = 2.12 Å and Sb–Ph_C (C17) = 2.14 Å, Table 1]. The proposition was examined by covalently tethering Ph_A to a neighbouring phenyl ligand, in an attempt to prevent reductive elimination. This was achieved by attempting the mono-*O*-phenylation of **2** with the bidentate 2,2′-biphenyl analogue **9** (Fig. 3). In

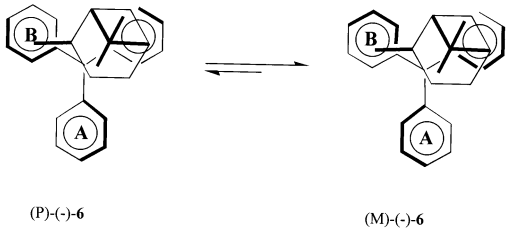


Fig. 5. The conformational diastereoisomers (P)-(−)-**6** and (M)-(−)-**6**.

[3] Hartree–Fock at the 3-21G(*) level using PC Spartan Pro (1.0.5). Designed and distributed by Wavefunction, Inc., 18401 Von Karman, Suite 370, Irvine, CA 92612, USA.

[4] The 3-21G(*) basis set is particularly appropriate for organic molecules incorporating main group elements such as phosphorus. For simplicity therefore, the antimony atom within the structure of **6** was replaced by phosphorous, and ΔE should be viewed as an upper limit.

the event of complex **9** forming a spiro TBPY diolate species reminiscent of **7** (Fig. 1), ligand transfer of axial Ph_A would prove impossible.

A search of the CSD for five co-ordinate spiro group V complexes possessing both a 2,2′-biphenyl and another bidentate ligand revealed three structural alternatives **10**–**12** (Fig. 6). Several P (V) and Sb (V) based TBPY systems of type **10** are observed, in which the bidentate ligands occupy the axial–equatorial co-ordination sites with the mono-dentate ligand occupying the remaining equatorial site {P (V); X = Ph, Me [23], α-napthyl [24], thienyl [25]), and Sb (V); X = tolyl [26]}. This arrangement clearly represents a structural precedent for an axially tethered Ph_A ligand. Two examples of SP co-ordination geometries are reported, both of which are based upon P (V). Here, a monodentate phenyl ligand occupies either an equatorial (**11** [27]) or axial (**12** [28]) co-ordination site. As discussed previously, regiochemical observations support a TBPY transition-state. As expected, and in contrast with $BiPh_3(OAc)_2$ **1**, phenylbiphenyl-2,2′-ylenebismuth diacetate **9** (Fig. 3) failed to mono-*O*-phenylate (−)-**2** or *cis*/*trans*-cyclohexane-1,2-diols. This is entirely consistent with the formation of a transition structure of type **10**, in which the favoured axial phenyl ligand is prevented from undergoing a reductive elimination because of a covalent tether.

In conclusion, reductive elimination of **1** upon exposure to strong ambient light results in the mono-*O*-phenylation of (−)-**2** at a faster rate than, (a) photoreduction to **8** or (b) reduction to $BiPh_3$ with concomitant oxidation of (−)-**2** to **4**. Structural studies support the model of David and Thieffry, which proposes that a dioxo TBPY transition structure reminiscent of **7** undergoes reductive elimination of an axial phenyl ligand. Finally, antimony complex **6**, a model for the dioxo

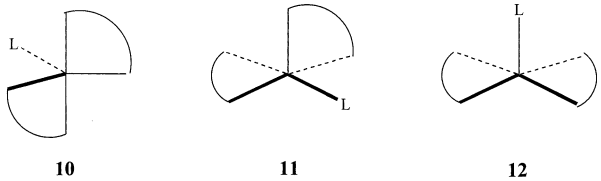


Fig. 6. X-ray crystallographically determined alternatives for spiro Group V complexes **10**–**12**.

TBPY transition structure **7**, constitutes the first example of an enantiopure complex incorporating a stereogenic XPh_3 propeller moiety. The complex adopts the energetically favoured (M)-(−) conformational diastereoisomer, which constitutes the lowest energy arrangement on the potential energy profile of the complex.

4. Experimental

4.1. General procedures

All reactions were performed under an atmosphere of dry nitrogen. CH_2Cl_2 was distilled under an atmosphere of nitrogen from CaH_2. ^{1}H-NMR were recorded on a JEOL JNM 300 (300 MHz) spectrometer, using $CDCl_3$ or CD_2Cl_2 as solvents, and referenced to residual $CHCl_3$ or CH_2Cl_2, with chemical shifts being reported at δ (ppm) from Me_4Si. ^{13}C-NMR were recorded on JEOL JNM 300 (75 MHz) spectrometer using $CDCl_3$. UV analyses were conducted on a Perkin–Elmer Lambda 40 spectrophotometer. Elemental analyses were conducted by the University of Warwick analytical services.

4.2. Preparations

4.2.1. (1R,2R,3S,5R)-3-Phenoxypinane-2-ol (3)

In bright sunlight, 1.1 equivalents of $BiPh_3(OAc)_2$ was added portionwise to a rapidly stirred solution of pinanediol in CH_2Cl_2 (0.2 M) under an atmosphere of N_2. After 1 h the heterogeneous solution was filtered, concentrated in vacuo and purified (SiO_2/$CHCl_3$) to afford a clear oil characterised as **3** (79%). Anal. Calc. for $C_{16}H_{22}O_2$: C, 78.1; H, 8.9. Found: C, 78.0; H, 8.7%. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): 7.30 (2H, m,. *o*-H), 6.97 (3H, m, *m*/*p*-H), 4.54 (1H, q, H-3), 3.68 (1H, s, OH), 2.56 (1H, m, H-4), 2.26 (1H, m, H-7), 2.07 (1H, t, H-1), 1.98 (1H, m, H-5), 1.80 (1H, dq, H-4), 1.64 (1H, t, H-7), 1.34 (3H, s, Me-9), 1.31 (3H, s, Me-10), 1.02 (3H, s, Me-8). ^{13}C-NMR (100 MHz, $CDCl_3$, 298 K): 157.6 (*i*-C), 129.7 (*o*-C), 121.7 (*m*-C), 116.3 (*p*-C), 75.9 (C-3), 73.8 (C-2), 53.8 (C-1), 40.5 (C-5), 38.5 (C-6), 35.6 (C-4), 30.7 (C-9), 28.4 (C-7), 28.0 (C-10), 24.5 (C-8).

4.3. Structural characterisation of 6

$C_{28}H_{31}O_2Sb$, $M_r = 260.64$, orthorhombic, space group $P2_12_12_1$, $a = 8.3694(2)$, $b = 11.1720(2)$, $c = 25.7117(6)$ Å, $U = 2404.12(9)$ Å^3, $T = 120(2)$ K, $Z = 8$, μ(Mo–K$_\alpha$) = 1.365 mm^{-1}, $F(000) = 1064$, 15 037 reflections were collected, θ range 1.99–27.46° (index ranges; $h = -9$ to 10, $k = -13$ to 14 and $l = -33$ to 33), which merged to give 5239 unique reflections ($R_{int} = 0.0473$) to refine against 284 parameters. Final R indices were $wR_2 = 0.0566$ and $R_1 = 0.0285$ [$F^2 > 2\sigma(F^2)$] and 0.0353 and 0.0597, respectively, for all data. Residual electron densities were 0.875 and −0.752 e Å^{-3}. Data were collected using a crystal of size $0.28 \times 0.20 \times 0.10$ mm on an Enraf Nonius Kappa CCD area detector diffractometer at the window of a rotating anode FR591 generator, with a molybdenum target [$\lambda_{(Mo-K_\alpha)} = 0.71069$ Å] and controlled by the Collect [29] software package. Images of 2° thickness and 10 s exposure were taken for a combined phi and omega scan strategy, with a detector to crystal distance of 30 mm (theta offsets between 3.9 and 6.2°) and processed by DENZO [30]. Data were corrected for absorption using the semi-empirical method employed in SORTAV [31]. The structure was solved by direct methods (SHELXS-97 [32]) and then subjected to full-matrix least-squares refinement based on F_o^2 (SHELXL-97 [32]). Non-hydrogen atoms were refined anisotropically with hydrogens included in idealised positions (C–H distance = 0.97 Å) with thermal parameters riding on those of the parent atom. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$.

4.4. Data retrieval

Crystal structures were located within version 5.21 (April 2001 release) of the Cambridge Structural Database (CSD) which contained 233 218 entries using the QUEST program [33].

5. Supplementary material

Crystallographic data for the structural analysis of **6** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 189161. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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