structure (excluding hydrogens) resulting from preliminary refinement to a conventional crystallographic discrepancy factor of $R = 16.2\%$, based on 535 intensities with $I_N > 2\sigma(I)$.

Despite the less bulky nature of the $ClCH_2CH_2NH$ moiety compared to the $(Cl_2CH_2CH_2)_2N$ group, the conformation of **2** in the solid state is the same as that of **1.** At this stage of refinement, detailed comparisons of the bond lengths of **2** to those of **1** are not warranted; however, no unusual deviations in these parameters are apparent at this time. As is the case with virtually all $P-NR_2$ systems including **1** and **3,** the angles around both nitrogens in **2** suggest trigonal planar nitrogen geometries. With but one exception, solution studies on phosphorinane systems of type **5a** and **5b** indicated that the dominant solution conformer is also that found in the solid state as revealed in nine X-ray studies.[7] Solution spectroscopic and dipole moment measurements are underway in an effort to clarify the conformational character of **1–3** in solution.

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Preparation of (*R*)- and (*S*)-Mevalonic Acids

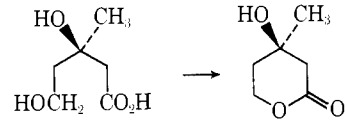
Sir:

We report new, simple syntheses[1] of (*R*)- and (*S*)-mevalonic acids by a combination of enzymatic and chemical procedures. The methods offer the particular advantages of utilizing readily available starting materials and enzyme preparations, and further deomonstrate the usefulness of biochemical systems as *organic* chiral reagents in asymmetric synthesis.

It has been shown that α-chymotrypsin hydrolyzes the pro-*S* ester group of dimethyl β-hydroxy glutarate.[2] We have treated β-hydroxy-β-methyl dimethyl glutarate (**2**) with α-chymotrypsin, and obtained the (3*S*)-half ester **3a** of high optical purity (see below). However, the rate of hydrolysis was slow and virtually a stoichiometric amount of the enzyme was required. In contrast, pig liver esterase (purchased from Sigma Co.) hydrolyzed **2** more efficiently and the same half ester (**3a**) of high optical purity was formed. In a typical experiment, **2** (400 mg) in 0.1 *M* phosphate buffer (pH 8.0) (7 ml), was incubated with the esterase (432 units) at 25° for 3 hr. Following the usual work-up **3a** (218 mg; 62%), $[\alpha]^{26}D$ +0.72 (CH_3OH), was obtained, and its absolute configuration and optical purity were determined by conversion to mevalonolactone.

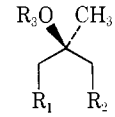
Reduction of **3a** with either $LiBH_4$[3] or Na in liquid ammonia–ethanol[4] afforded (*R*)-mevalonolactone (**4**) in yields of 81 and 73%, respectively. Both samples of **4** were converted to their benzhydrylamide derivatives which had identical physical constants:[5] mp 98–99°, $[\alpha]^{26}D$ −2.79° (EtOH). Since $LiBH_4$ and $Na-NH_3$ are known to reduce selectively carboxylic esters but not carboxylic acids,[3,4] it follows that the pig liver esterase cleaved the pro-*R* methyl ester group of **2** giving **3a.**

2 **3a**



4

It is worthy of note that when **3a** was treated with diborane at 0° for 1 hr, it also gave (*R*)-mevalonolactone (41%) (benzhydrylamide, mp 97–98°, $[\alpha]^{26}D$ −1.98 (EtOH)) (71% optical purity). Since it is generally accepted that diborane reduces preferentially carboxylic acids,[6,7] this could indicate that the pig liver esterase has hydrolyzed the pro-*S* methyl ester group of **2.** If correct, the finding would contradict the conclusions derived from the above $LiBH_4$ and $Na-NH_3$ experiments. The anomaly was clarified when the 3-acetoxy derivative (**3c**), $[\alpha]^{26}D$ −0.42 (CH_3OH) (obtained from **3a**), was reduced with diborane. In this instance, (*S*)-mevalonolactone (benzhydrylamide, mp 98–99°, $[\alpha]^{26}D$ +2.78 (EtOH)) was obtained. This confirmed the (**3a**) structure and hence the stereospecific hydrolysis of the pro-*R* methyl ester group of **2** by pig liver esterase. The reason for this abnormal behavior is not clear, but the results do clearly show that the presence of the free hydroxyl function at C-3 interfered with the normal course of borane reduction.



1, $R_1 = R_2 = CH_2OH$; $R_3 = H$
2. $R_1 = R_2 = CO_2Me$; $R_3 = H$
3a, $R_1 = CO_2Me$; $R_2 = CO_2H$; $R_3 = H$
b. $R_1 = CO_2H$; $R_2 = CO_2Me$; $R_3 = H$
c, $R_1 = CO_2Me$; $R_2 = CO_2H$; $R_3 = Ac$

An alternative approach to the synthesis of mevalonolactone was based on the ability of *Flavobacterium oxydans* to oxidize a wide variety of gem hydroxymethyl compounds to

the corresponding hydroxymethylcarboxylic acids.[8] We tested the ability of the enzyme system of this organism to stereoselectively oxidize one of the enantiotopic hydroxyethyl groups attached to a prochiral center in **1**.[9,10] When **1** (300 mg) was incubated with lyophylized cells (360 mg) of *F. oxydans* at pH 6.5 for 72 hr, (*S*)-mevalonolactone (46 mg) $[\alpha]^{26}D$ +21.8° (EtOH) was obtained. This result could be interpreted as indicative of the preferential oxidation of the pro-*S* hydroxyethyl grouping of **1** by *F. oxydans*. However, exposure of (3*RS*)-mevalonolactone (120 mg) to the organism afforded (*S*)-mevalonolactone (44 mg) $[\alpha]^{26}D$ +15° (EtOH) and suggested that (*R*)-mevalonolactone was selectively utilized by the enzyme system. The selective utilization of (*R*)-mevalonolactone by microorganisms has been noted before.[11] At present, the pathway of oxidation with *F. oxydans* is not clear and can be interpreted in several ways. (a) *F. oxydans* oxidized preferentially the pro-*S* hydroxyethyl group of **1**, thereby affording the (*S*)-mevalonolactone. (b) *F. oxydans* oxidizes both the pro-*R* and pro-*S* hydroxyethyl of **1** to give (±)-mevalonolactone. The organism then selectively uses up the (*R*)-mevalonolactone leaving behind the (*S*) enantiomer which is isolated.[11]

Further experimentation is required for the determination of the mechanism of oxidation by *F. oxydans*.[12]

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Synthesis and Characterization of the Fluxional Species $H_2Os_3(CO)_{10}L$. The Crystal Structure of $H_2Os_3(CO)_{11}$

Sir:

Recent work has established that the formally electron-deficient cluster compound $H_2Os_3(CO)_{10}$ is much more reactive than the saturated cluster $Os_3(CO)_{12}$ toward olefins and acetylenes.[1] In order to examine the initial state of interaction between an electron donor and $H_2Os_3(CO)_{10}$ without the complications of subsequent hydrogen transfer reactions, we have treated $H_2Os_3(CO)_{10}$ with several simpler σ-donor/π-acceptor ligands. We now report that the adducts thus formed display unique structural and dynamic features in that they each contain one bridging and one terminal hydride ligand which undergo mutual exchange.

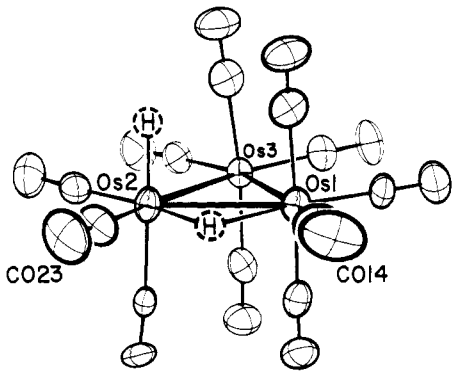

Figure 1. General view of the $H_2Os_3(CO)_{11}$ molecule, showing the probable hydrogen sites. Note that the axial H and CO on Os(2) have a 63.8%:36.2% disorder.

Addition of a two-electron donor ligand to a purple hexane solution of $H_2Os_3(CO)_{10}$ causes a rapid color change to yellow.[2] From these solutions yellow, crystalline compounds of formula $H_2Os_3(CO)_{10}L$ (L = CO (**1**), CNMe (**2**), PPh_3 (**3**), PMe_2Ph (**4**), $AsMe_2Ph$ (**5**)) have been isolated and fully characterized by elemental analysis and by ir, NMR, and mass spectra. The compounds are moderately stable to ambient conditions both as solids and in solution, although **1** in solution slowly reverts to $H_2Os_3(CO)_{10}$ in the absence of carbon monoxide. Molecular ions are observed in the mass spectra of **1**, **2**, and **5**, but the highest mass ion observed for **3** and **4** is $(M - CO)^+$. Additional features of the mass spectra together with solution ir spectra indicate that triangular structures (as determined for $H_2Os_3(CO)_{10}$[3]) terminal carbonyls only, and lack of symmetry characterize this set of compounds.

In addition to the appropriate ligand ^1H NMR resonances, at −60°, each adduct displays two equally intense signals for the hydride ligands, one near τ 20, the other near τ 30 ($J_{H-H} \sim 4$ Hz).[4] These signals are assigned to a terminal and to a bridging hydride ligand, respectively, by comparison with available chemical shift data for other saturated hydridoosmium compounds.[5] Furthermore, bands at 1930 (w, $\Delta\nu_{1/2} \sim 20$ cm^{-1}) and 1525 cm^{-1} (vw, $\Delta\nu_{1/2} \sim 50$ cm^{-1}) appearing in the ir spectrum (KBr) of solid $H_2Os_3(CO)_{11}$ shift to 1410 (vw, $\Delta\nu_{1/2} \sim 25$ cm^{-1}) and 1110 cm^{-1} (vw, $\Delta\nu_{1/2} \sim 40$ cm^{-1}) for $D_2Os_3(CO)_{11}$. The higher-frequency band may be assigned as primarily a terminal Os–H(D) stretching mode,[7] whereas the lower-frequency band must arise from vibration of a bridged Os–H(D)–Os structure.[6]

The detailed structure of $H_2Os_3(CO)_{11}$ has been determined by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 8.0744 (16) Å, b = 14.7265 (29) Å, c = 14.7770 (28) Å, β = 101.36 (1)°, V = 1722.7 (6) Å^3, and ρ(calcd) = 3.396 g cm^{-3} for Z = 4 and mol wt = 880.73. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer using Mo Kα radiation and a θ–2θ scan technique. The structure was solved by using the Os coordinates of $Os_3(CO)_{12}$[8] as the starting point for the usual structure-factor, least-squares refinement, difference-Fourier synthesis, iterations. All data were corrected for the effects of absorption (μ = 221.5 cm^{-1}; T = 0.166–0.307). All non-hydrogen atoms were accurately located, the final discrepancy indices being R_F = 3.68% and R_{WF} = 3.52% for the 2259 reflections with $2\theta < 45°$ (none rejected). There is a slight disorder problem with the axial ligands on