Registry No. 1, 20004-62-0; **2**, 82544-89-6; **3**, 82544-90-9; **3** cyclohexylimine, 82544-91-0; **4**, 82544-92-1; **5**, 95-65-8; **6**, 82544-93-2; **7**, 82544-94-3; **8**, 82544-95-4; **9**, 82544-96-5; **10**, 82544-97-6; **11**, 82544-98-7; **13**, 74460-84-7; **14**, 82544-99-8; **15**, 82545-00-4; **16**, 82545-01-5; **17**, 82545-02-6; **18**, 82554-90-3; **19**, 82545-03-7; **20**, 82545-04-8; **21**, 82545-05-9; **22**, 82545-06-0; diethylcarbamoyl chloride, 88-10-8; ethyl acetoacetate, 141-97-9; 3,5-dimethoxybenzaldehyde, 7311-34-4.

Supplementary Material Available: Spectral and analytical data for compounds **1**, **3** and cyclohexylimine thereof, **4**, **7**, **11**, **13–15**, and **19–22** (2 pages). Ordering information is given on any current masthead page.

"Triple-Decker Sandwich" with a Planar As$_5$ Ring. Synthesis and Crystal Structure of CpMo[μ-(η^4-As$_5$)]MoCp

Arnold L. Rheingold,* Michael J. Foley, and
Patrick J. Sullivan

Department of Chemistry, University of Delaware
Newark, Delaware 19711

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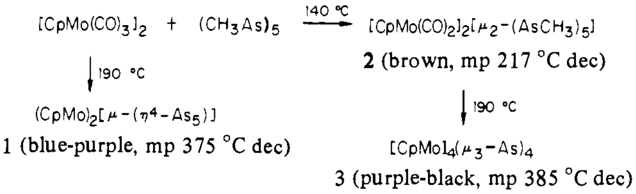
Unusual configurations of homoatomic main-group catenates can be stabilized by coordination to transition-metal centers. The generation of novel structures containing arsenic atom catenates has been particularly fruitful due to a convenient balance between bond energies low enough to allow facile transformations and high enough to confer sufficient stability for isolation of both intermediates and final products. Structures containing organically substituted linked arsinidene fragments, RAs, have been reviewed by West.[1] We now report the preparation and crystallographic characterization of the first transition-metal complex containing a ring of five unsubstituted arsenic atoms in a triple-decker sandwich structure, CpMo[μ-(η^4-As$_5$)]MoCp (**1**).

Complex **1** is one member of a series of cluster products obtained from reactions of *cyclo*-(AsCH$_3$)$_5$ and [CpMo(CO)$_3$]$_2$, as shown in Scheme I. [CpMo(CO)$_2$]$_2$(AsCH$_3$)$_5$ (**2**) is obtained after 4 days as a brown, crystalline solid in high yield (>50%) from equimolar quantities of reactants in dilute toluene solution in a sealed tube at 140 °C.[5] The same reactants at 190 °C for 2 days produce **1** in somewhat lower yield (20–30%).[6] Since both **1** and **2** contain the same 2Mo/5As ratio, we tested the reasonable assumption that **1** was derived from **2**; however, heating isolated samples of **2** at 190 °C for 2 days in toluene produced only **3**.[7]

Scheme I



2 (brown, mp 217 °C dec)

1 (blue-purple, mp 375 °C dec)

3 (purple-black, mp 385 °C dec)

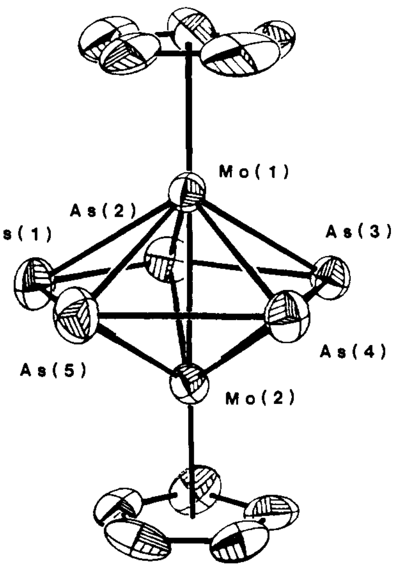


Figure 1. Molecular geometry and labeling scheme for (CpMo)$_2$[μ-(η^4-As$_5$)] (**1**). Hydrogen atoms have been omitted, and thermal elipsoids are drawn at the 50% probability level.

Table I. Selected Bond Distances and Angles for [CpMo]$_2$[μ-(η-As$_5$)] (**1**)[a]

	Bond Distances (Å)		
Mo(1)-Mo(2)	2.764 (2)	As(4)-Mo(2)	2.577 (2)
As(1)-Mo(1)	2.721 (2)	As(5)-Mo(1)	2.571 (2)
As(1)-Mo(2)	2.731 (2)	As(5)-Mo(2)	2.551 (2)
As(2)-Mo(1)	2.549 (2)	As(1)-As(2)	2.397 (3)
As(2)-Mo(2)	2.553 (2)	As(2)-As(3)	2.751 (3)
As(3)-Mo(1)	2.541 (2)	As(3)-As(4)	2.570 (2)
As(3)-Mo(2)	2.554 (2)	As(4)-As(5)	2.762 (3)
As(4)-Mo(1)	2.580 (2)	As(5)-As(1)	2.389 (2)
	Bond Angles (deg)		
As(5)-As(1)-As(2)	107.8 (1)	Mo(1)-As(1)-Mo(2)	61.2 (1)
As(1)-As(2)-As(3)	112.0 (1)	Mo(1)-As(2)-Mo(2)	65.6 (1)
As(2)-As(3)-As(4)	104.4 (1)	Mo(1)-As(3)-Mo(2)	64.7 (1)
As(3)-As(4)-As(5)	103.0 (1)	Mo(1)-As(4)-Mo(2)	65.7 (1)
As(4)-As(5)-As(1)	112.7 (1)	Mo(1)-As(5)-Mo(2)	65.6 (1)
av	108.0 (1)	av	64.6 (1)

[a] Data are for the configuration shown in Figure 2. Deviations between independent molecules, except as noted in the text, are not significant.

Blue-purple (nearly black) crystals of **1** belong to the monoclinic space group $P2_1/c$, with a = 14.884 (5) Å, b = 12.639 (3) Å, c = 15.576 (5) Å, β = 90.50 (3)°, D_c = 3.16 g cm^{-3}, and Z = 8 (two independent molecules form the asymmetric unit). The final R_F value was 0.043 on the basis of 2435 independent observed reflections with $I \geq 3\sigma(I)$ (3.5° ≤ 2θ ≤ 45°, Mo Kα).

The molecular configuration of **1**, as determined at 23 °C, is shown in Figure 1, and selected bond distances and angles are given in Table I. The two independent molecules differ only in the rotational orientation of one Cp ring to the other two rings. All rings are essentially eclipsed in one molecule (see Figure 2); in the other molecule, one Cp ring is rotated 22° relative to the other eclipsed rings. No other structural parameters show significant differences between molecules.

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(1) West, B. O. In "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements"; Rheingold, A. L., Ed.; Elsevier; Amsterdam, 1977; p 409.

(2) Two examples of structures containing three-membered arsenic rings are known: Co(CO)$_3$As$_3$[3] and [(triphos)Co]$_2$As$_3$(BPh$_4$)$_2$.[4]

(3) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5631.

(4) Di Vaira, M.; Midollini, S.; Sacconi, L.; Zanobini, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 676.

(5) Complex **2** contains a 1,5-*catena*-(AsCH$_3$)$_5$ bridge symmetrically linking both CpMo(CO)$_2$ units without metal-metal bonding. Rheingold, A. L.; Churchill, M. R., submitted to *J. Organomet. Chem.*

(6) Mass spectral data (**1**): M$^{+\cdot}$ = base peak, m/e = 695 (all other peaks ≤17.0% of base).

(7) Structural characterization of **3** is incomplete. Elemental and mass spectral analysis support the formula (CpMoAs)$_4$, and the crystallographic arrangement of As and Mo atoms is unambiguously displayed as a cubanelike structure symmetrically equivalent to the structure of [(CO)$_3$FeAsCH$_3$]$_4$ (Röttinger, E.; Vahrenkamp, H. *J. Organomet. Chem.* **1981**, *213*, 1). Complex **3** crystallizes in the cubic space group $P\bar{4}3n$, which imposes a disordered threefold rotational axis along the CpMo···As vector. Preparation and characterization of the methylcyclopentadienyl derivative will, we hope, reduce crystallographically demanded symmetry.

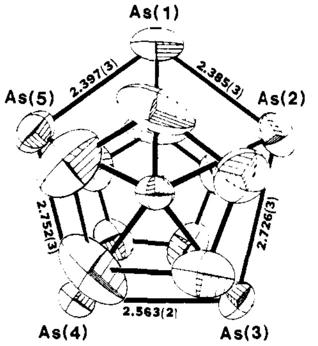

Figure 2. 1 viewed along the Mo–Mo vector. The displacement of the intersection of this vector with the As_5 plane away from As(1) is evident in this view. The large variation in As–As bond distances allows the partitioning of the As_5 system into μ-(η^2-As_3) and μ-(η^2-As_2) ligands.

Although **1** clearly is in appearance a triple-decker sandwich complex (the three rings are coplanar, deviation $\leq 2.3°$), many features of the bonding of the central As_5 ring to the Mo atoms argue against a strict application of the bonding descriptions for triple-decker sandwiches developed by Hoffmann et al.[8] For instance, in contrast to all known and hypothesized triple-decker sandwiches discussed by Hoffmann et al.,[8] **1** possesses a short metal–metal vector (2.764 (2) Å) through the central ring. This distance is intermediate between those observed for Mo–Mo single bonds, 2.9–3.2 Å,[9] and those for Mo=Mo double bonds, ~2.6 Å.[10]

We have found it more productive to consider **1** as an analogue of a growing list of compounds characterized by two transition-metal centers bridged by main-group 6 atoms displaying within individual complexes two or more bridging geometries.[10a,11-13] In the majority of these dinuclear complexes, most or all of the bridging atoms lie on a plane perpendicular to and bisecting the metal–metal vector. An examination of the As–As and Mo–As bond distances in **1** reveals many similarities to these sulfur-bridged complexes (Table I and Figure 2). All of the As–As distances deviate significantly from the "normal" single-bond length of 2.42–2.44 Å.[14] The two shortest As–As distances, As(1)–As(2) = 2.397 (3) Å and As(1)–As(5) = 2.389 (2) Å, are similar to the As–As distances in $Co(CO)_3As_3$, 2.372 (5) Å,[3] and $[Cr(CO)_5]_3As_2(C_6H_5)_2$, 2.371 Å,[15] for the latter compound an As=As double bond is proposed. The remaining As–As distances are all longer than normal. As(2)–As(3), 2.726 (3) Å, and As(4)–As(5), 2.752 (3) Å, are particularly long, suggesting a fractional bond order ($\sim{}^1/_2$) and allowing a convenient partitioning of the As_5 ring into two fragments: As(5), As(1), and As(2) comprising a μ-(η^2-As_3) ligand, and As(3)–As(4) a μ-(η^2-As_2) ligand. The variations in Mo–As bond distances are informative in an analysis of the bonding of the As_2 and As_3 ligands to the metal atoms. The two Mo–As(1) distances, average 2.73 Å, are longer than the remaining Mo–As distances, which range from 2.54 to 2.58 Å (Table I). While few standards for Mo–As bond distances are available, the Mo–As distances in **2** average 2.63 Å;[5] this figure also agrees well with other "normal" Mo–As distances we have recently determined. The displacement away from As(1) of the intersection of the Mo–Mo vector and the As_5 plane is particularly evident in Figure 2. Thus, it would be appropriate to compose a primary Mo–As bonding scheme involving just the four terminal As atoms [As(2), As(3), As(4), and As(5)]. Such a view is consistent with the structures of the many polysulfur-bridged dinuclear group 6B metal, which appear limited to a maximum of four bridging atoms.[10a,10d,11-13] A particularly dramatic example is the complex $(C_5Me_5)_2Cr_2S_5$,[13] although five sulfur atoms lie on a plane perpendicular to and bisecting the Cr–Cr bond, one S atom is excluded from metal coordination through the formation of an iso-μ-[η^1-(S_2)] ligand.[11]

We propose, therefore, to account for electron distribution in **1** in the following way: it is a Mo(III) complex, i.e., $CpMo^{2+}$, of the ions $[\mu\text{-}(\eta^2\text{-}As_3)]^{2-}$ and $[\mu\text{-}(\eta^2\text{-}As_2)]^{2-}$ or, alternatively, of the ion $[\mu\text{-}(\eta^4\text{-}As_5)]^{4-}$. The four electrons added to As_5 to form the $As_5{}^{4-}$ ion are distributed one each to the four terminal As atoms, making them formally isoelectronic with sulfur. Dahl has discussed a molecular orbital scheme for the isoelectronic complex $[CpMo(SMe)_2]_2$,[10d] which we believe is also relevant to **1**. Transannular and circumannular nonbonding pair delocalization within the As_5 ring may contribute additional donor orbitals for metal bonding not found in the isoelectronic sulfur complexes and may, therefore, account for the cyclic bridging atom geometry found in **1**. In keeping with the formalisms developed by Dahl,[10d] we would assign a bond order of 2 to the Mo–Mo bond. The Mo=Mo bond distance in **1** is considerably longer than those cited earlier;[10] 2.764 (2) Å as compared to an average of ~2.6 Å. This may be accounted for by a combination of the in-plane outward displacement of the bridging atoms in **1** due to the larger atomic size of As and an apparent minimum metal–(bridge atom)–metal bond angle of ~65° found in this and similar complexes.

Further verification of the assigned electron distribution is the observation that **1** is an odd-electron, paramagnetic complex coupled with the preliminary determination that the unpaired spin is localized on an As atom, presumably As(1).

Although we prefer this analysis to one based upon the molecular orbital schemes for triple-decker sandwich complexes developed by Hoffmann et al.,[8] we see a clear compatibility in the two viewpoints. Hoffmann has observed that 30- and 34-electron configurations are particularly stable for triple-decker sandwiches. If the $(As_5)^{4-}$ group is a 12-electron donor and each $CpMo^{2+}$ group contributes 9 electrons, the total is 30; if 4 electrons are associated with the Mo=Mo bond, the total is 34.

The loss of methyl groups from arsenic, as required to form complexes **1** and **3**, appears to be a metal-catalyzed process. Although toluene solutions of pure *cyclo*-$(AsCH_3)_5$ begin to undergo complex oligomerization reactions at 190 °C, no evidence for loss of organic substitution is found, e.g., formation of elemental arsenic. The preparation of $Co(CO)_3As_3$ from $(CH_3As)_5$ and $Co_2(CO)_8$ occurs under conditions similar to those for **1**.[3]

Acknowledgment. This work was supported by a grant from the National Science Foundation. We are grateful to the Climax Molybdenum Corp. for their generous donation of molybdenum hexacarbonyl and to Robert Richman, Carnegie-Mellon Institute, for helpful discussions regarding bonding.

Supplementary Material Available: Positional and thermal parameters with estimated standard deviations, calculated hy-

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(8) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, 98, 3219.

(9) (a) $[CpMo(CO)_3]_2$, 3.235 (1) Å: Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086. (b) $[(CO)_3(Et_3P)Mo(PMe_2)]_2$, 3.090 (2) Å: Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1735. (c) $[MeC_5H_4MoS_2]_2$, 2.991 (1) Å, $[Me_5C_5MoS_2]_2$, 2.905 (1) Å: DuBois, M. R.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. (d) $\{Mo_2(CO)_2[P(OMe)_3](S\text{-}t\text{-}Bu)_3(C_7H_7)\}$, 2.946 (2) Å: Benson, I. B.; Knox, S. A. R.; Naish, P. J.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2235.

(10) (a) $[MeC_5H_4Mo(S)SMe]_2$, 2.582 (1) Å: DuBois, M. R.; VanDerveer, M. C.: Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456. (b) $[CpMo(CO)(S\text{-}t\text{-}Bu)]_2$, 2.616 (2) Å: Benson, I. B.; Killops, S. D.; Knox, S. A. R.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1137. (c) $[Mo_2(CO)_3(C_2Ph_2)(C_5Ph_4O)(C_4Ph_4)_2]$, 2.618 (1) Å: Potenza, J. A.; Johnson, R. J.; Chirico, R.; Efraty, A. *Inorg. Chem.* **1977**, *16*, 2354. (d) $[CpMo(MeS)_2]_2$, 2.603 (2) Å: Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7470.

(11) The structure of $(MeC_5H_4)_2V_2S_5$ displays three S-bridging geometries, μ-S, μ-(η^1-S_2), and μ-(η^2-S_2), and possesses a V–V bond (2.658 (1) Å). The μ-S and μ-(η^2-S_2) bridging atoms are on a plane bisecting the V–V vector. Bolinger, M. C.; Rauchfuss, T. B.; Rheingold, A. L. submitted to *Organometallics*.

(12) $(Me_5C_5)_2Cr_2S_5$ contains three types of S ligands with all five S atoms in a plane between the two Cr atoms. The Cr–Cr distance, 2.489 (2) Å, is consistent with a bond order of two.[13]

(13) Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1765.

(14) Gatehouse, B. M. *J. Chem. Soc., Chem. Commun.* **1969**, 948. Donohue, J. *Acta Cryst.* **1962**, *15*, 708.

(15) Huttner, G.; Schmid, H.-G.; Frank, A.; Orama, O. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 234.

drogen atom parameters, and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

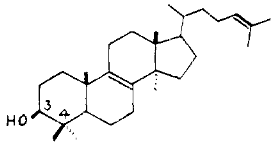
Mechanism-Based Inactivation of 4-Methylsterol Oxidase by 4α-(Cyanomethyl)-5α-cholestan-3β-ol

Désirée L. Bartlett and Cecil H. Robinson*

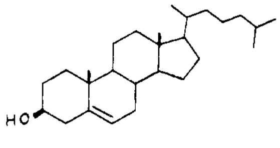
Department of Pharmacology and
Experimental Therapeutics
The Johns Hopkins University, School of Medicine
Baltimore, Maryland 21205

Received May 10, 1982

An important part of cholesterol biosynthesis in rat liver is the removal of the 4,4-dimethyl groups of lanosterol as CO_2, through oxidative demethylation. We report here the first mechanism-based inactivator of this key enzymatic process.



lanosterol

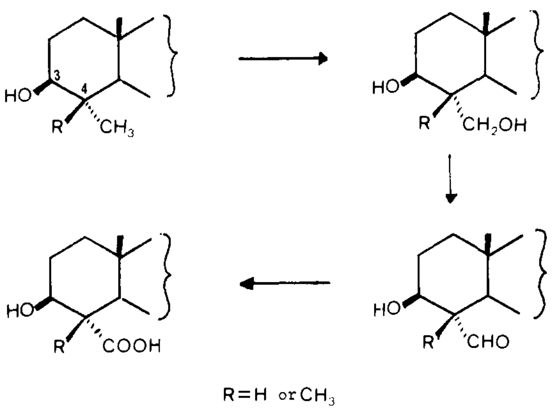


cholesterol

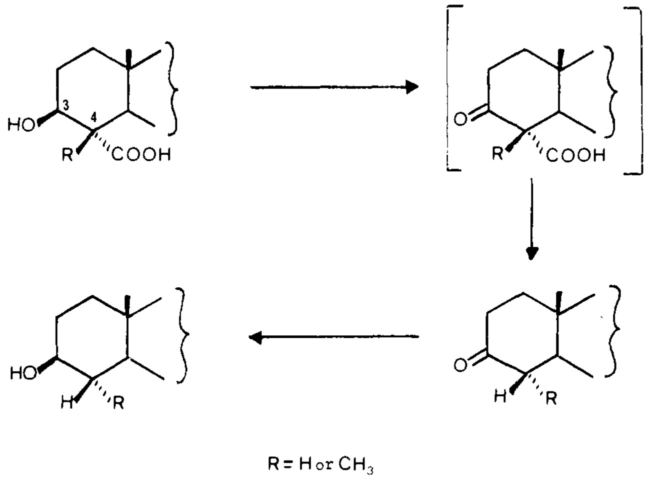
The enzyme-catalyzed oxidative loss of the 4,4-dimethyl grouping in lanosterol has been the subject of extensive studies,[1] including the use of model substrates such as 4,4-dimethyl- and 4α-methyl-5α-cholest-7-en-3β-ol and the corresponding 7,8-dihydro compounds.[2] These investigations led to the proposals summarized in Schemes I and II. Thus the rat liver microsomal system termed 4-methylsterol oxidase catalyzes the oxidation of the 4α-methyl group in either a 4,4-dimethyl or a 4α-methyl substrate to, successively, the 4α-hydroxymethyl, 4α-formyl, and 4α-carboxylic acid grouping (Scheme I). Each of these steps requires 1 mol equiv each of NAD(P)H and oxygen, and the rate of oxidation appears to increase with each successive step. The oxidation of the 4α-methyl group to the corresponding 4α-carboxylic acid occurs rapidly with no accumulation of intermediates. The demethylation process is then completed by an NAD^+-linked dehydrogenase/decarboxylase, via the β-keto acid (Scheme II).[3]

The microsomal 4-methylsterol oxidase system that converts the 4α-methyl group to a 4α-carboxy group is an NAD(P)H–O_2-requiring system but appears not to be a cytochrome P-450 dependent complex. We have devised a mechanism-based inactivator for 4-methylsterol oxidase, based on the reaction sequence of Scheme I and using the rationale shown in Scheme III. It was hoped that the enzymatically catalyzed hydroxylations normally occurring at the 4α-methyl group might generate the electrophilic acyl cyanide grouping from the 4α-cyanomethyl analogue **1**. Reaction of this enzyme-generated electrophile with a nucleophilic residue at the enzyme's active site could then lead to inactivation of the enzyme via covalent bond formation.

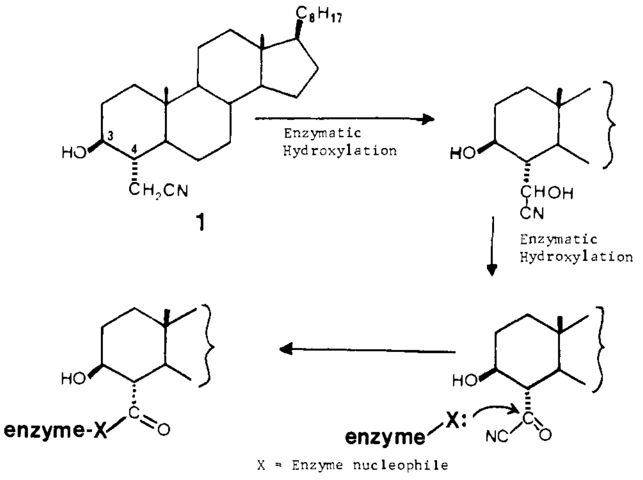
Scheme I



Scheme II



Scheme III



The hitherto undescribed 4α-cyanomethyl compound (**1**) was synthesized[4] via 3β-benzyloxy-4α-(hydroxymethyl)-5α-cholestane (**2**), mp 122–123.5 °C, derived in turn from the known[5] 4α-(carbomethoxy)-5α-cholestan-3β-ol (**3**) by benzylation, followed by $LiAlH_4$ reduction. Thus, compound **2** was converted to the *p*-toluenesulfonate (pyr–TsCl). Treatment with NaCN/DMF/acetone followed by removal of the 3β-benzyloxy group (Pd/C–H_2) then gave the desired 4α-(cyanomethyl)-5α-cholestan-3β-ol (**1**): mp 188–189 °C (acetone); IR ($CHCl_3$) 3630, 3460, 2240 cm^{-1}; NMR (300 MHz) δ 3.45 (m (7), 1, 3α-H), 2.90 (dd, $J = 17, 4$ Hz, 1, CH_2CN), 2.46 (dd, $J = 17, 4$ Hz, 1, CH_2CN); mass spectrum, m/e 427 (M^+), 412, 287, 272.

Our enzymatic studies, carried out with rat liver microsomal

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(4) Newly described compounds showed appropriate IR, NMR, and mass spectra. Compounds **1** and **4** showed correct elemental analyses.

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