

The Crystal Structure of Senaite

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Senaite from the Diamantina region of Brazil crystallizes in the rhombohedral space group $R\bar{3}$ with lattice parameters $a_{rh} = 9.172$ (1) Å and $\alpha = 69.020$ (5)°. The equivalent hexagonal parameters are $a_{hex} = 10.393$ (2) and $c_{hex} = 20.811$ (5) Å. Its formula, determined from microprobe analysis data is $Pb_{0.80}Ti_{13.66}Fe_{0.49}Mn_{1.08}O_{38}$. The structure was solved using 573 'observed' [$I^2 \geq 3\sigma(I^2)$] symmetry independent reflexions collected on a Philips PW1100 diffractometer using Mo $K\alpha$ radiation and refined to an R value of 0.077. The structure is based on a nine-layer ($hhc\dots$) close-packed array of anions with lead atoms partially occupying one of the thirteen anion sites in the cubic layers. Metal atoms occupy nineteen of the available octahedral sites and two of the tetrahedral sites in the unit cell. The octahedra articulate to give two basic structure building units, a trigonal grouping of three edge-shared octahedra and a 6-member hexagonal ring of edge-shared octahedra. The trigonal triads link further by edge sharing into 12-member hexagonal rings. The tetrahedra and an octahedron link the 6-member and 12-member rings *via* corner sharing. The metal atoms are ordered in the structure.

Introduction

Senaite, crichtonite, and davidite form a closely related series of minerals with similar morphologies and chemical compositions and with almost identical X-ray powder diffraction patterns. Strunz (1966) has grouped the three minerals together and assigned to them the general composition $X_2Y_5O_{12}$ where Y = small cations, Ti^{4+} and Fe^{3+} , and X = large cations. The minerals differ most significantly in the distribution of X , which corresponds to Fe^{2+} , Ce^{3+} , U^{4+} in davidite, Fe^{2+} , Mn^{2+} , Pb^{2+} in senaite, and Fe^{2+} , Mn^{2+} , Sr^{2+} in crichtonite.

All three minerals are found in close association with ilmenite in nature, and several researchers (Hussak & Reiting, 1903; Shawe, 1953; Pabst, 1961) considered them to have structures closely related to ilmenite. Thus davidite is usually found in intimate oriented intergrowth with ilmenite and rutile (Contag, 1962), and senaite occurs in diamond-bearing conglomerates containing ilmenite, rutile, magnetite, and other minerals (Freise, 1930). Recently, Haggerty (1970/71) has reported crichtonite as an oxidation product of ilmenite in Hawaiian basalt lava lakes. Single-crystal X-ray structure studies on senaite and davidite (Pabst, 1961; Rouse & Peacor, 1968) show that these two minerals have almost identical trigonal cells with $a_{hex} \approx 10.4$ and $c_{hex} \approx 20.9$ Å. Their structures were shown to be based on a nine-layer close-packed oxygen framework with the largest cations (Pb in senaite and U, Ce in davidite) situated on anion sites in the framework. However, the various researchers

were unable to establish the positions of the other metal atoms, mainly iron and titanium, and so the detailed structures remained unsolved.

As part of a structural study programme on close-packed oxides related to ilmenite (Grey & Reid, 1975) we are studying the structural relations between davidite, senaite, and crichtonite and report here the results of a structure determination for senaite.

Experimental

Crystals of senaite from the Diamantina region of Brazil (U.S. National Museum, Mineralogy Division, #R7241) were provided by John S. White Jr. The results of a microprobe analysis on one of the crystals are given in Table 1. A number of crystals were initially examined by Weissenberg and precession techniques to check that they were single phase and free from twinning. The photographic film data confirmed the unit cell and space group reported by Rouse & Peacor (1968), *i.e.* trigonal $R\bar{3}$ or $R3$, with rhombohedral dimensions, $a_r = 9.17$ Å and $\alpha = 69.0^\circ$.

For the intensity data collection a pear-shaped crystal with maximum diameter 0.083 mm and length 0.13 mm was mounted along its long dimension (= [001] in the hexagonal cell), on a Philips PW 1100 4-circle automatic diffractometer. Thirteen high-angle reflexions provided the 2θ values used to calculate the lattice parameters reported in Table 1. Intensities were collected with graphite monochromated Mo $K\alpha$ radiation with a take-off angle of 12.18° . A θ - 2θ scan, 3 - 25° , was used with a variable scan width given by $\Delta\theta = (1.2 + 0.3 \tan \theta)$ and a speed of $0.05^\circ \text{ s}^{-1}$. Two background measurements, each for half the scan time, were made for each scan, one at the lower and one at

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Table 1. *Microprobe analysis and unit-cell data for senaite*

Microprobe analysis (wt. %)	
Ti	34.41
Fe	19.05
Mn	3.16
Pb	8.72

Chemical formula, corrected to 38 O:
 $\text{Pb}_{0.80}\text{Ti}_{13.66}\text{Fe}_{6.49}\text{Mn}_{1.08}\text{O}_{38}$

Unit-cell parameters, trigonal $R\bar{3}$

$a_{\text{rh}} = 9.172$ (1) Å	$a_{\text{hex}} = 10.393$ (2) Å
$\alpha_{\text{rh}} = 69.020$ (5)°	$c_{\text{hex}} = 20.811$ (5)
$V_{\text{rh}} = 648.89$ Å ³	
$Z_{\text{rh}} = 1$	
$d_{\text{calc}} = 4.59$ g cm ⁻³	
$\mu = 140.4$ cm ⁻¹	

the upper limit. The intensities were processed using a program written for the PW 1100 diffractometer by Hornstra & Stubbe (1972). Although we were unable to apply an accurate absorption correction because of the complex shape of the crystal, a partial compensation was achieved by averaging the intensities of equivalent reflexions in the rhombohedral cell. Thus the 2252 reflexions measured were reduced to an averaged unique set of 660 reflexions. Of these 87 were considered to be statistically insignificant ($I \leq 3\sigma[I]$) and were given a zero weight during the refinement.

Scattering factor curves for Mn, Fe, Pb, Ti, and O were taken from *International Tables for X-ray Crystallography* (1962). The curve for lead was corrected for anomalous dispersion. All computing was performed on the Monash University CDC 3200 and the CSIRO CDC 7600 computers.

Solution and refinement of the structure

The lack of any significant difference in intensities of Friedel pairs, in spite of the considerable amount of lead present, suggested a centrosymmetric space group. A three-dimensional Patterson map was then com-

puted in $R\bar{3}$, and it indicated that the lead atom was at the origin. From a consideration of Pb-M vectors the positions of the metal atoms were determined, and a positional refinement of these atoms followed by a difference Fourier revealed the presence of all oxygens. A least-squares refinement of all atom positions and isotropic temperature factors was carried out, giving an R of 0.13. At this stage the lead temperature factor was +1.5, while those for all other atoms were negative. To correct the scaling problem, the temperature factors of *all* atoms were set at +0.25 and the lead multiplier was refined. Using the new value for the lead multiplier, a refinement of all atom positions and temperature factors was carried out, resulting in an R of 0.09. A study of the temperature factors of the metal atoms, as well as bond length data calculated at this stage, indicated ordering of the Ti, Mn, and Fe atoms. A new set of composite scattering curves for the different metal atom sites was calculated which was consistent with the chemical analysis given in Table 1. A full matrix refinement of all positional and thermal parameters, and the lead multiplier, gave an R value of 0.078. As expected, the lead multiplier and temperature factor correlated strongly in this refinement, and the resulting values, 0.83 and 2.14, must be considered with reserve. However, the lead occupancy agrees closely with the value of 0.80 obtained from the chemical analysis (Table 2). Also the high temperature factor, although unexpected, is similar to those observed for partially occupied sites in other structures, e.g. Moore & Araki (1974). A series of manual refinements using values surrounding those given above failed to produce agreement as good as that of the above refinement. The final parameters are given in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31502 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

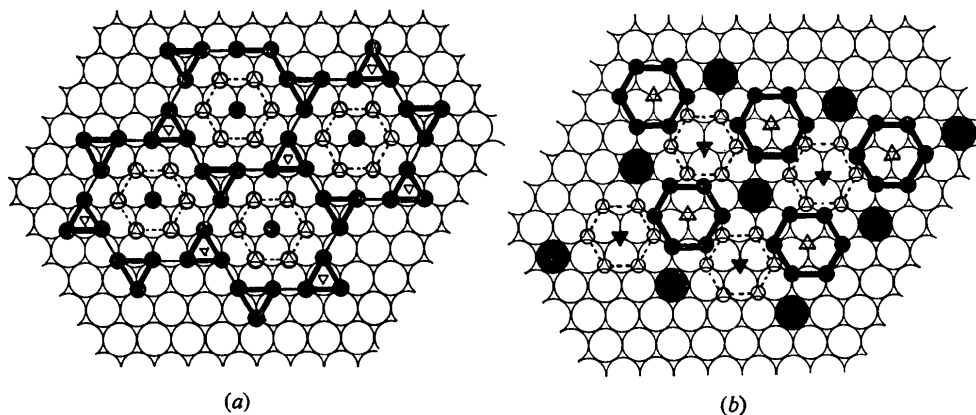


Fig. 1. Arrangement of metal atoms above (●) and below (○) (a) a hexagonal anion layer and (b) a cubic anion layer. The large open circles are oxygens, while the large filled circles are lead. The triangles represent metals in tetrahedral sites. Full and dashed lines join pairs of metal atoms which share octahedral edges.

An independent solution in $P\bar{1}$ was also carried out to satisfy a doubt that equivalent reflexions in $R\bar{3}$ were different by an amount greater than that expected from absorption effects. The resulting model showed no deviations from $R\bar{3}$ symmetry.

Table 2. *Senaite*: final atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^2$)

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
M(0)	0.83 Pb	0	0	0	213 (9)
M(1)	1.00 Mn	5000	5000	5000	47 (12)
M(2)	2.00 Fe	3101 (2)	3101 (2)	3101 (2)	53 (9)
M(3)	1.66 Ti				
	+4.34 Fe	3486 (4)	190 (4)	1263 (4)	43 (5)
M(4)	6.00 Ti	3076 (5)	1494 (5)	7184 (5)	62 (6)
M(5)	6.00 Ti	4737 (5)	6412 (5)	840 (5)	58 (6)
O(1)	6.00 O	3013 (17)	3771 (17)	6280 (17)	71 (25)
O(2)	6.00 O	1492 (17)	9413 (17)	2394 (17)	64 (24)
O(3)	6.00 O	9176 (19)	3030 (19)	4590 (19)	105 (25)
O(4)	6.00 O	1426 (18)	9909 (18)	5127 (18)	101 (26)
O(5)	6.00 O	3933 (21)	1339 (21)	4874 (21)	167 (32)
O(6)	6.00 O	7091 (17)	718 (17)	2453 (17)	85 (24)
O(7)	2.00 O	2134 (10)	2134 (10)	2134 (10)	158 (52)

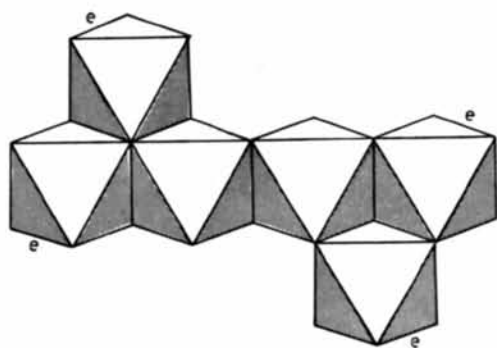


Fig. 2. Polyhedral representation of the basic structural unit in the h -M- h layer.

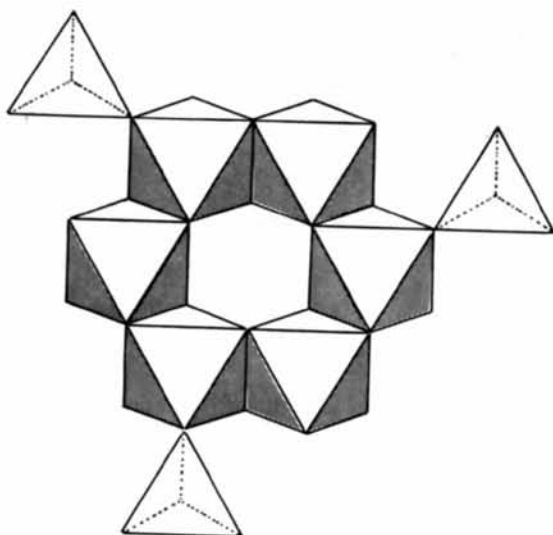


Fig. 3. Polyhedral representation of the structural unit in the h -M- c layer, comprising a hexagon of edge-shared octahedra, corner sharing to three tetrahedra.

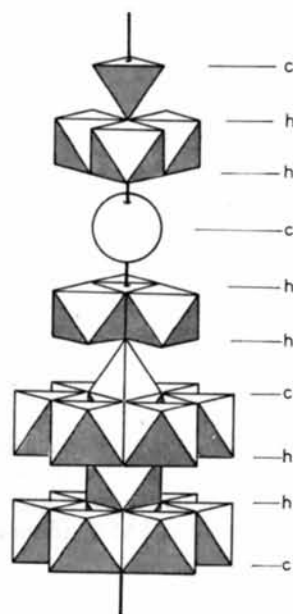


Fig. 4. Polyhedral diagram showing the stacking of octahedra and tetrahedra along the trigonal axis for *senaite*. The circle represents lead. The anion layer stacking sequence is shown.

Description of the structure

The structure of *senaite* is based on a close-packed anion framework with a nine-layer stacking sequence ($hhc\dots$) and with lead atoms partially occupying one of the thirteen anion sites in the cubic layers. There are two types of cation layers, illustrated in Fig. 1. Metal atoms occupy seven of the available thirteen *octahedral* sites between pairs of hexagonal anion layers (*i.e.* h -M- h) in the unit cell, whereas six of the octahedral sites and one of the tetrahedral sites between adjacent hexagonal and cubic anion layers (h -M- c) are occupied per unit cell. The basic structure building unit in the h -M- h metal atom layer is a pair of trigonal triads of edge-shared octahedra, shown in Fig. 2. The triad pairs link by sharing edges (marked e in Fig. 2) to generate the large 12-member hexagonal rings shown in Fig. 1(a). An isolated metal-oxygen octahedron at the centre of each hexagonal ring completes the h -M- h type metal layer. In the h -M- c metal atom layer, six octahedrally coordinated metals link by edge-sharing into hexagonal rings. Each hexagon crosslinks to six others by corner-sharing with the basal oxygen atoms of three tetrahedra. A hexagon of edge-shared octahedra and its associated three tetrahedra are shown in Fig. 3. The relationship between adjacent layers of metal atoms is illustrated in Fig. 1. Across a hexagonal anion layer, octahedra share corners only [Fig. 1(a)], whereas across a cubic anion layer the octahedra share only edges [Fig. 1(b)]. The linking of tetrahedra and octahedra between layers is shown in Fig. 4. The oxygen common to the three shared edges of each trigonal triad forms the vertex of an octetra-

hedral site. The tetrahedron links by corner sharing *via* its basal oxygens to the hexagon of edge-shared octahedra in the layer below. Fig. 4 also shows the disposition of the Pb atoms and the octahedrally coordinated metal M(1) along the threefold axis.

Interatomic distances

In senaite, divalent lead partially occupies one of the thirteen anion sites in the cubic close-packed layers. The lead atom sites lie on the trigonal axis ([111] in the rhombohedral cell), and there is very little distortion of the anion lattice around them. As shown in Table 3, the average O–O distance for the surrounding oxygens is 2.86 Å, which is close to the value for the average O–O distances within the close-packed layers, $=a_{\text{hex}}/\sqrt{13}=2.88$ Å. The average Pb–O distance is somewhat shorter, at 2.82 Å, which agrees quite well with the sum of their ionic radii, 2.85 Å (Shannon & Prewitt, 1969).

In senaite there is an ordering of the smaller metal ions (Ti^{4+}) into the octahedral sites within the *h*–*M*–*c* layers, whereas the larger metal ions occupy the octahedral sites in the hexagonally close packed layers, *h*–*M*–*h*. This is apparent from the interatomic distances shown in Table 3. Average M–O distances for M(4) and M(5) in the *h*–*M*–*c* layers compare very closely with the mean Ti–O bond length of 1.96 Å for the three TiO_2 minerals rutile, anatase, and brookite (Baur, 1961). Although the increase in the average M–O distance for M(3), relative to M(4) and M(5), is scarcely outside the associated errors, the M(3)–O average, 2.00 Å, is in excellent agreement with the value of 1.995 Å calculated for $(\text{Fe}_{0.25}^{3+}\text{Ti}_{0.75}^{4+})\text{O}$ using the ionic radii tables of Shannon & Prewitt (1969). The remaining metal atom site between the hexagonally close-packed oxygen layers, M(1), is occupied by Mn^{2+} . The mean M(1)–O distance of 2.23 Å corresponds very closely to the average Mn^{2+} –O distance observed in manganese-containing minerals, *e.g.* in leucophoeni

Table 3. Bond lengths for senaite (Å)

M(1) octahedron		M(2) tetrahedron		Pb site	
M(1)–O(1) [6]	2.227*	M(2)–O(5) [3]	1.991	Pb–O(2) [6]	2.786
		–O(7)	2.012	–O(6) [6]	2.849
		mean	1.996	mean	2.817
O(1)–O(1) ¹ [6]	3.078	O(5)–O(5) [3]	3.296	O(2)–O(2) ¹ [6]	2.752
–O(1) ¹¹ [6]	3.221	–O(7) [3]	3.220	O(2)–O(6) [12]	2.912
mean	3.149	mean	3.258	O(6)–O(6) [6]	2.867
				mean	2.860
M(3) octahedron		M(4) octahedron		M(5) octahedron	
M(3)–O(4)	1.945	M(4)–O(2)	1.911	M(5)–O(1)	1.847
–O(3)	1.985	–O(1)	1.939	–O(4)	1.887
–O(4) ¹	1.991	–O(3)	1.960	–O(3)	1.918
–O(2)	1.994	–O(6)	1.988	–O(6)	1.993
–O(7)	2.020	–O(5)	2.017	–O(5)	2.021
–O(2) ¹	2.054	–O(6) ¹	2.043	–O(5) ¹	2.118
mean	1.998	mean	1.976	mean	1.964
O(4)–O(4) ¹	2.65	O(1)–O(6)	2.55	O(5)–O(5) ¹	2.53
–O(2)	2.68	O(5)–O(3)	2.55	–O(3)	2.55
O(7)–O(2)	2.68	–O(6)	2.60	O(6)–O(1)	2.55
–O(2) ¹	2.68	–O(1)	2.70	–O(5)	2.60
O(2)–O(4) ¹	2.75	O(2)–O(6)	2.78	O(1)–O(5)	2.78
O(4)–O(7)	2.79	O(1)–O(3)	2.84	O(4)–O(5)	2.79
–O(3)	2.85	O(6)–O(1) ¹	2.87	O(3)–O(5) ¹	2.82
–O(2) ¹	2.86	O(2)–O(1)	2.89	–O(4)	2.85
O(4) ¹ –O(3)	2.86	–O(3)	2.89	O(1)–O(4)	2.86
O(3)–O(7)	2.91	–O(6)	2.91	–O(3)	2.92
–O(2)	3.02	O(6) ¹ –O(3)	2.91	O(5) ¹ –O(4)	2.94
O(4) ¹ –O(2) ¹	3.07	–O(5)	2.99	–O(6)	2.96
mean	2.82	mean	2.79	mean	2.76
Metal–metal distances					
M(1)–M(4) <i>c</i>	3.632	M(2)–M(5) <i>c</i>	3.397	Pb–M(4)	3.395
–M(5) <i>c</i>	3.793	–M(4) <i>c</i>	3.494	–M(3)	3.846
		–M(3) <i>c</i>	3.494		
M(3)–M(3) ¹ <i>e</i>	2.912	M(4)–M(5) <i>e</i>	2.953	M(5)–M(5) <i>e</i>	3.278
–M(3) ¹¹ <i>e</i>	3.024	–M(5) ¹ <i>e</i>	3.049		
–M(3) ¹¹ <i>e</i>	3.025	M(4)–M(5) <i>e</i>	3.081		
–M(4) <i>c</i>	3.444				
–M(5) ¹ <i>c</i>	3.473				
–M(4) ¹ <i>c</i>	3.537				
–M(5) ¹¹ <i>c</i>	3.629				
–M(4) ¹¹ <i>c</i>	3.613				

* Standard deviations for M–M, M–O and O–O are 0.005, 0.017 and 0.023 Å respectively.

cite, $\text{H}_2\text{Mn}_7\text{Si}_3\text{O}_{14}$, $\text{Mn}-\text{O}_{\text{av}}=2.22 \text{ \AA}$ (Moore, 1970). Similarly $\text{O}-\text{O}_{\text{av}}$ for the oxygens associated with M(1) in senaite, 3.15 \AA , compares closely with an $\text{O}-\text{O}_{\text{av}}=3.12 \text{ \AA}$ in leucophoenicite. The coordination around the Mn atom in senaite is almost perfect octahedral, with six equivalent Mn-O distances, and with a variation in the O-Mn-O angles from 87.4 to 92.6° .

The mean M-O distance for the tetrahedrally coordinated metal atom M(2) is 2.00 \AA . This value is very close to the sum of the ionic radii for tetrahedrally coordinated Fe^{2+} and O^{2-} , *i.e.* 2.01 \AA (Shannon & Prewitt, 1969) and agrees with the value of 2.00 \AA found for $(\text{Fe}^{2+}-\text{O})_{\text{tet}}$ in titanomagnetite (Stout & Bayliss, 1975). The coordination polyhedron around M(2) is very regular with angles O-M(2)-O in the narrow range 107.0 to 111.7° and with apical and basal M(2)-O distances equal within experimental error. The three largest metal ions, Pb^{2+} , Mn^{2+} , and Fe^{2+} , are all ordered into sites on the trigonal axis (Fig. 4), and all have very regular coordination polyhedra. On the other hand, the largest distortions in the structure are associated with the smallest cations, Ti^{4+} , in the M(4) and M(5) sites. The distortion of the M(5)- O_6 octahedron is much greater than that for the M(4)- O_6 octahedron; the degree of distortion is related to the type and symmetry of the articulated polyhedra. Thus M(4)- O_6 shares edges with three other octahedra and corners with four octahedra and one tetrahedron and has $\Delta\text{M}-\text{O}=0.13 \text{ \AA}$ and $\Delta\text{O}-\text{M}-\text{O}=17.51^\circ$. The M(5)- O_6 octahedron shares edges with four octahedra and corners with four octahedra and two tetrahedra. Its range of metal-oxygen distances and oxygen-metal-oxygen angles is 0.27 \AA and 26.44° respectively.

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The Crystal and Molecular Structure of μ -Chloro-di- μ -phenylthio-di[hydridobis(triphenylphosphine)iridium(III)] Perchlorate

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μ -Chloro-di- μ -phenylthio-di[hydridobis(triphenylphosphine)iridium(III)] perchlorate crystallizes with three molecules of acetone in space group $P2_1$ with $a=15.013$ (3), $b=12.918$ (1), $c=22.044$ (4) \AA , $\beta=91.94$ (1) $^\circ$, $Z=2$. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares calculations to final values of R and R_w of 0.050 and 0.070 for 7564 observed reflexions. The molecule contains two Ir atoms bridged by a Cl [Ir-Cl=2.558 (2) \AA] and by the S atoms of two phenylthiol ligands [mean Ir-S=2.407 (7) \AA]. The remaining three sites on each approximately octahedrally coordinated Ir atom are filled by two triphenylphosphine groups [mean Ir-P=2.329 (3) \AA] and a hydride.

Introduction

The dimeric iridium(III) hydride complex $[\text{IrHCl}(\text{SPh})(\text{PPh}_3)_2]_2$ (1) (Herdé & Senoff, 1973) reacts

with chloroform or dichloroethane to form an off-white powder (2) whose structure could not be elucidated by standard chemical techniques. Reaction of (1) with AgClO_4 in acetone under reflux, followed by