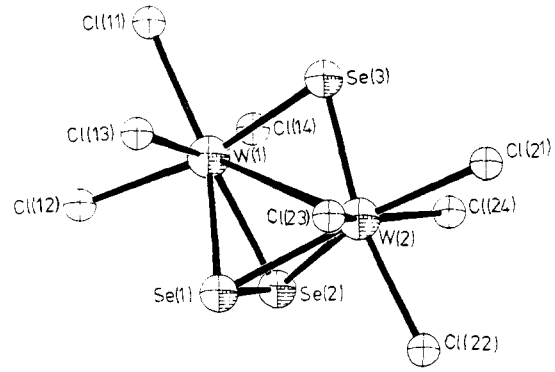

Figure 1. The structure of the $[W_2Cl_8Se(Se_2)]^{2-}$ ion.

above background were used in the final refinement which led to a conventional R factor of 0.0838. The tungsten, selenium, and chlorine atoms were refined anisotropically and the thermal parameters exhibited no noteworthy characteristics.

The asymmetric unit contains two $[AsPh_4]^+$ cations and a $[W_2Cl_8Se_3]^{2-}$ anion (Figure 1). Both metal aroms are bonded to four chlorine atoms and are linked by a bridge consisting of a selenium atom, Se(3), and also an Se_2 group. The anion has approximate C_s symmetry, with the mirror plane containing W(1), W(2), Cl(11), Cl(12), Cl(21), Cl(22), Se(3), and the mid-point of the Se(1)-Se(2) bond. The geometric arrangement around the tungsten atoms of four chlorine atoms, Se(3), and the midpoint Se(1)-Se(2) is approximately octahedral.

The distance between the two tungsten atoms (2.862 (3) Å) suggests the presence of a single metal-metal bond (cf. distances in $[W_3O_2(O_2CR)_6]^{2+}$ (2.75 Å)[6] and $(Et_2NCS_2)(MeO)_2W$-$(\mu$-$S)_2$-$W(MeO)_2(S_2CNEt_2)$ (2.791 (1) Å[7]) to which single bonds have been assigned). Further support for the metal-metal bond is given by the acute angle subtended at the bridging selenium atom Se(3) (73.3 (2)°) (cf. 73.2 (1)° seen in the W(V)-S-W(V)-S fragment[7]).

The tungsten-selenium (Se(3)) distances (2.384 (7)Å to W(1), 2.409 (7) Å to W(2)) are shorter than expected when the tungsten-sulfur distances in $(Et_2NCS_2)(MeO)_2W$-$(\mu$-$S)_2$-$W(MeO)_2(S_2CNEt_2)$ (2.360 (4), 2.319 (4) Å) and the interatomic distances in elemental sulfur (2.012 to 2.087 Å[8]) and selenium (2.375 (5)[9]) are considered. The tungsten to Se_2 group distances are all in the range 2.558 (6) to 2.580 (6) Å.

We have been unable to find literature reports of structures containing a bridging Se_2 group, but examination of the difference between the molybdenum-sulfur distances in the bridges Mo-$(\mu$-$S)_2$-Mo (2.298 (2) to 2.344 (2) Å[10]) and Mo-$(\mu$-$S_2)$-Mo (2.40-2.46 Å[11]) are in accord with the difference between the W-Se(3) and W-Se_2 distances observed here.

The selenium-selenium distance (2.255 (8) Å) is shorter than that seen in Na_2Se_2 (2.38 (5) Å[12]). This shortening of the interatom distance on coordination of Se_2^{2-} is exactly parallel to the changes seen in the disulfide ion which has an interatom distance of 2.13 (5) Å in the ionic compound Na_2S_2[12] that becomes 1.98 Å in $Mo_2Cl_4Cl_{4/2}$-$(\mu$-$S_2)_2$[11], 2.035 (6) to 2.063 (6) Å in $(S_2)_2Mo$-$(\mu$-$S_2)_2$-$Mo(S_2)_2$,[2,13] and 2.03 in Mo_3Cl_4-S-$(\mu$-$S_2)_3$.[11] The valence shell configuration of Y_2^{2-} (Y = S or Se) is $(\sigma s)^2$ $(\sigma^* s)^2$ $(\sigma p)^2$ $(\pi)^4$ $(\pi^*)^4$ and so, when Y_2^{2-} bonds side onto two metal atoms with suitable empty d orbitals π^* to d_π, donation can take place, with a shortening of the Y···Y bond length.

The tungsten-chlorine distances (2.418 (13) to 2.481 (14) Å) are within the range of known tungsten(V)-chlorine terminal bonds. The two independent cations were ordered and the angles between the phenyl rings ranged from 45.5 to 89.1°.

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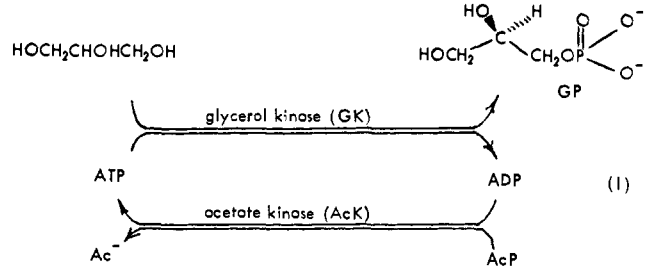
Enzymatic Synthesis of *sn*-Glycerol 3-Phosphate[1]

Sir:

We describe here a practical procedure for the synthesis of *sn*-glycerol 3-phosphate (GP, L-glycerol 3-phosphate) based on enzymatic phosphorylation of glycerol using ATP and glycerol kinase (E.C. 2.7.1.30) (eq 1). The ATP is regenerated



using the recycling system described previously,[2] with acetyl phosphate (AcP) as the ultimate phosphorylating agent.[3] GP is an important intermediate in syntheses of phospholipids.[4] Present preparations of chiral glycerol derivates are based on isolation from natural sources,[5] or on cleavage of the C-3-C-4 bond of derivatives of mannitol.[6] Both types of procedure are capable of generating substantial amounts of materials, but require several steps. The enzymatic synthesis described here requires only a single step, and provides what is probably the most practical method presently available for the preparation of quantities of enantiomerically pure GP.

A representative synthesis was carried out in a 5-L round-bottomed flask equipped with a pH electrode and containing a magnetic stirring bar and 5 g of nylon beads to facilitate stirring. The flask was charged with 1 L of doubly distilled water containing glycerol (110 mmol), ATP (2 mmol), $MgCl_2$·$6H_2O$ (4 mmol), and dithiothreitol (DTT, 10 mmol).[7]

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The solution was adjusted to pH 7.6 (no buffer). Polyacrylamide gel particles containing immobilized glycerol kinase (42 U, 30 mL of gel) and acetate kinase (E.C. 2.7.2.1, 42 U, 7 mL of gel) were added to the mixture.[8] An aqueous solution (60 mL, 1 M, pH 7.6) containing 120 mmol of diammonium acetyl phosphate[3] was added continuously to the stirred reaction mixture over 48 h at a rate of 2.5 mL/h (2.5 mmol/h).[9] The mixture was maintained between pH 7.4 and 7.8 by addition of 1.5 M NH_4OH, using an automatic pH controller. Reaction was carried out at ambient temperature, and the reaction mixtures and all reagent solutions were deoxygenated before use and maintained under argon. After addition of 120 mmol of AcP over 48 h, enzymatic assay[10] indicated that 100 mmol of GP had been formed. Stirring was stopped and the gel suspension allowed to settle for 6 h at ambient temperature. The supernatant was decanted under positive argon pressure using a stainless-steel cannula. The reactor was then reloaded with glycerol, ATP, DTT, and $MgCl_2$ and the addition of AcP continued for another 48 h. Three consecutive reactions (134 h of operation) generated a total of 318 mmol of GP. The combined supernatant from these reactions (3810 mL) was adjusted to pH 3.0 with concentrated HCl and concentrated under vacuum (10 Torr, 60 °C) to a volume of 40 mL. This concentrate was adjusted to a pH between 0.0 and 0.5 with concentrated HCl and 120 mL of methanol was added. The mixture was allowed to stand for 20 min at 4 °C, the precipitate (mainly inorganic phosphate) separated by filtration, and the filtrate treated with 2 equiv of cyclohexylamine (63 g, 636 mmol).[11] Any precipitate which formed at this point was separated by filtration and discarded. The mixture was poured slowly into 1000 mL of acetone with vigorous stirring. The resulting white, fluffy precipitate was filtered and washed with acetone (2 × 500 mL) and anhydrous ether (500 mL). The precipitate (115 g) was dried over Drierite for 12 h under vacuum: it contained 95% di(cyclohexylammonium) GP (238 mmol, 79% based on AcP, 76% based on glycerol). The activities of GK and AcK in the recovered gel after these three consecutive runs were 98 and 51%, respectively, of the activities of the original immobilized preparations.

This same enzymatic system has been used to prepare *sn*-glycerol-2-d_1 3-phosphate in 0.5-mol scale (213 g of the dicyclohexylammonium salt) and *sn*-glycerol-3-d_1 3-phosphate in 30-mmol scale.[12]

This synthesis illustrates the practicality of synthesizing chiral intermediates by enzymatic reactions which require ATP. The requirement for substantial amounts of isotopically and chemically substituted phospholipids in membrane biochemistry and the prospect that large quantities of enantiomerically pure phospholipids may be needed if liposomes prove useful as drug delivery systems justify the development of this synthesis of *sn*-glycerol 3-phosphate. A facile preparation of GP should also prove useful in syntheses of other substances (triglycerides, trichoic acids, cardiolipins)[5,13] derived from it biosynthetically.

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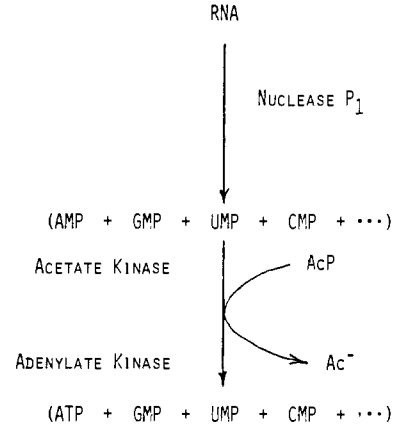
Conversion of the Adenosine Moieties of RNA into ATP for Use in Cofactor Recycling

Sir:

We report here a practical procedure for transforming the adenosine moieties of RNA into ATP (Scheme I). Yeast RNA and the requisite enzymes are commercially available and inexpensive, and diammonium acetyl phosphate (AcP) is easily prepared.[1] The mixture of nucleotides generated by this procedure (containing ATP, GMP, UMP, CMP, and other minor constituents) may be used without purification in synthetic schemes involving enzymatic catalysis with ATP recycling.[2,3] This method is the most practical one presently available for generating the ATP required in such schemes. The following details illustrate the manipulations involved in preparing the ATP-containing mixture, and in its use in ATP-requiring enzymatic synthesis.

In a representative procedure, RNA (100 g, 85% pure, from Torula yeast, Sigma Chemical Co.) was dissolved in 400 mL of water, and the solution adjusted to pH 5.6 with NaOH and to 0.1 mM in Zn(II).[4] Nuclease P_1[5] (E.C. 3.1.4.-, 0.20 mg, 93 U[6]) was added and the solution was allowed to stir at 65 °C.

Scheme I. Conversion of RNA into a Mixture of Nucleotides Containing ATP



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