Both temperature-programmed reaction and X-ray photoelectron data indicate that methoxide is the intermediate that gives rise to gaseous methyl radicals. After annealing to 500 K, a temperature near the onset of methyl radical formation, methoxide (285.7 eV) is the majority surface species. A species with a C(1s) binding energy of 282.9 eV is also present; this binding energy is the same as that of atomic carbon detected after annealing to 750 K, a temperature past all dihydrogen formation. The intensity of the 282.9-eV peak increases after annealing from 500 to 750 K by 20–60%. Adsorbed methyl would be expected to have a binding energy around 284 eV, on the basis of comparison with C(1s) data for other hydrocarbon species on Mo(110),[9-11] and to undergo strong irreversible bonding with molybdenum atoms. Formation of a significant amount of low-temperature dihydrogen during temperature-programmed reaction agrees with the presence of atomic carbon at 500 K. Also, high-temperature dihydrogen and methyl radical are formed with similar kinetics during temperature-programmed reaction above 500 K, supporting reaction of a common intermediate (methoxide) to form both products and in agreement with the observed increase in the 282.9-eV peak intensity after annealing to 750 K. Thus we assign the low binding energy species present at 500 K to atomic carbon or a partially dehydrogenated fragment. Since no reversible C–H bond activation is observed during reaction of coadsorbed CD_3O and CH_3O, the lower binding energy species cannot give rise to methyl radical via C–H bond formation. Only reaction of *methoxide* to gaseous methyl radical and high-temperature dihydrogen in a competing reaction pathway is consistent with these results.

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Registry No. Mo, 7439-98-7; CH_3O, 3315-60-4; O, 7782-44-7; CH_3OH, 67-56-1; CH_3, 2229-07-4.

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Phosphonium Ion Fragmentations Relevant to Organophosphonate Biodegradation

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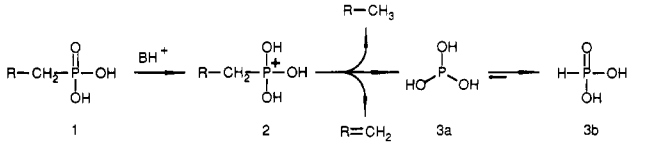
Microbial degradation of organophosphonates **1** via carbon to phosphorus (C–P) bond cleavage has prompted a rapid expansion in chemical literature[1,2] relevant to the biodegradation. However, the chemistry of organophosphonates under reducing conditions, particularly in regard to C–P bond cleavage, is still largely unknown. This report examines the single-electron and hydride reduction of organophosphonates and organotrineopentoxyphosphonium[3] trifluoromethanesulfonates **4a–e** (Table I) structurally related to organophosphonium ion **2** (Scheme I). A tremendous difference in reactivity of reductants with organophosphonium ions relative to organophosphonates has been discovered. This leads to the suggestion (Scheme I) of possible phosphonium ion **2** intermediacy during organophosphonate biodegradation. Phosphonium ion **2** reduction or eliminative cleavage of the organophosphonium C–P bond could produce alkanes and alkenes along with phosphite **3a**.

Scheme I



Scheme II

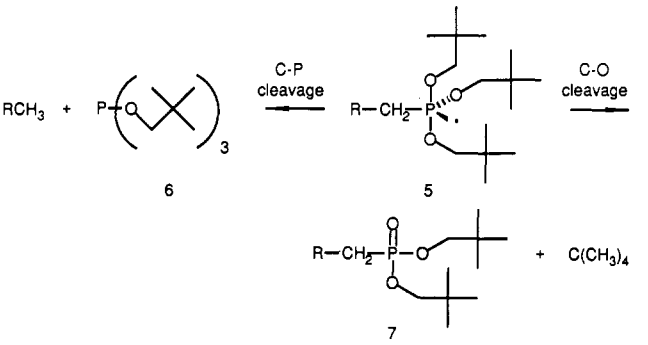
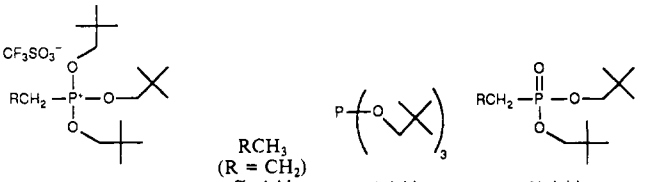


Table I[a]



4	RCH$_3$ (R = CH$_2$) % yield	%yield	%yield
a, R = H	1	2	91
b, R = CH_3	1	3	89
c, R = CH_3CH_2	1.1 (0.02)	4	89
d, R = CH_2=CH	6	22	70
e, R = C_6H_5	24	35	58

[a] A tetrahydrofuran solution of naphthalene radical anion was added dropwise to organophosphonium ions **4a–e** in tetrahydrofuran under nitrogen at room temperature. Addition was continued until a green color persisted. Volatiles (C1–C3) were analyzed by gas chromatography fitted with alumina F1 or Carbosphere columns. Solution components were separated by gas chromatography fitted with an OV-101 column. Gas chromatography yields were determined relative to an internal standard. Products were identified by coinjection and comparison of ^{31}P NMR chemical shifts with those of authentic samples.

Neither hydrocarbons nor phosphorus-containing products resulting from C–P bond cleavage are observed during naphthalene radical anion reactions with organophosphonate diesters. In contrast, addition of naphthalene radical anion to organotrineopentoxyphosphonium ions leads to instantaneous reaction with complete loss of starting phosphonium ion. Hydrocarbon[4] as well as phosphorus-containing products indicative of C–P bond cleavage (Table I) are observed.[5] The hydrocarbons[6] formed during C–P bond cleavage are reminiscent of the carbon fragments formed during *Escherichia coli* degradation of organophosphonates. Notably, *E. coli* degradation of propylphosphonic acid leads to

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(4) Propene formation could be due to eliminative C–P bond cleavage or alkyl radical disproportionation. The absence of products resulting from alkyl radical combination which competes with alkyl radical disproportionation suggests that propene arises primarily from eliminative C–P bond cleavage. Naphthalene dianion is probably functioning as the base. See ref 7a.
(5) The difference in hydrocarbon and trineopentylphosphite yield is likely a consequence of naphthalene radical anion trapping of alkyl radical. See: (a) Shafer, S. J.; Closson, W. D.; van Dijk, J. M. F.; Piepers, O.; Buck, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 5118. (b) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400.
(6) Ethene is also produced during single-electron reduction of **4b**. However, an undetermined proportion of the ethene is coming from tetrahydrofuran decomposition. No propene is generated during decomposition of tetrahydrofuran. See: Carnahan, J. C., Jr.; Closson, W. D. *J. Org. Chem.* **1972**, *37*, 4469.

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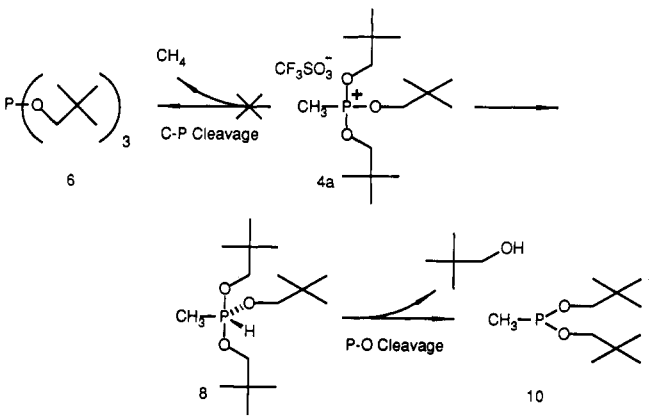
Scheme III



propane and propene with the alkane in substantial excess.[1a]

Phosphoranyl radical **5** is likely produced[7] by the single-electron reduction (Scheme II) leading to both carbon to oxygen (C–O) and C–P bond cleavage. On the basis of the yields of phosphorus-containing products (Table I), C–O and C–P bond cleavage are the only major reactions that occur during single-electron reduction of the phosphonium ions. Thermodynamically favored[8] C–O bond cleavage dominates the single-electron reductions. Carbon to phosphorus bond homolysis competes with C–O bond homolysis as the kinetically favored fragmentation when the resultant carbon-centered radical is stabilized as in the single-electron reductions of allyl- and benzyltrineopentoxyphosphonium ion. Low levels (1–3%) of trineopentyl phosphate are detected during all single-electron reductions of phosphonium ions.

Reaction with lithium triethylborohydride provides a gauge of organophosphonate and organophosphonium reactivity with a hydride reductant. Organophosphonate diesters are unreactive while methyltrineopentoxyphosphonium trifluoromethanesulfonate (**4a**) is rapidly reduced with complete loss of phosphonium ion.[9] Fragmentation via C–P bond cleavage was initially anticipated (Scheme III), given the precedented dealkylations observed during reaction of quaternary ammonium ions with hydride reagents.[10] However, no methane or trineopentyl phosphite is produced. Instead, a quantitative conversion to dineopentyl methylphosphonite (**10**) indicative of P–O bond cleavage (Scheme III) is observed. Suggestion of phosphorane **8** as an intermediate follows from reactions of phosphonium ions with nucleophiles which proceed through or produce phosphoranes.[11]

Mechanisms proposed for microbial cleavage of organophosphonate C–P bonds include organophosphonate oxidation to a phosphonyl radical[1] or reduction to an organophosphonite ($RCH_2P(OH)_2$) followed by phosphoranyl radical formation.[2] Organophosphonium ion intermediacy and C–P bond fragmentation (Scheme I) differs from these proposals by virtue of the phosphorus-containing metabolites predicted to form during biodegradation. Phosphonium ion but not phosphonyl radical intermediacy should lead to phosphorous acid as the immediate product of C–P bond cleavage. All reductive mechanisms postulate intermediacy of a phosphoranyl radical and a phosphorous acid. However, an organophosphonite is absent from Scheme I where phosphonium ion is directly reduced to phosphoranyl radical.

The chemistry of organophosphonates and organophosphonium ions under reducing conditions significantly expands the chemical data base relevant to organophosphonate C–P bond cleavage. Even hydride reduction of organophosphonium ions, which does not lead to C–P bond cleavage, provides potential insights. Organophosphonate stability toward hydride reduction relative to the facile reduction of phosphonium ion indicates how a biological system could catalyze organophosphonite formation. Phosphonium ion fragmentation can thus be considered as a new, free-standing mechanism (as in the case of single-electron reduction) or an adjunct (like hydride reduction) to an extant mechanism. Which is the correct viewpoint awaits identification of the phosphorus-containing metabolites present during organophosphonate biodegradation.

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(9) Lithium triethylborohydride in tetrahydrofuran was added dropwise under a nitrogen atmosphere to a tetrahydrofuran solution of **4a** at −78 °C. After quenching with water, product yield was determined by gas chromatography relative to decane as an internal standard. Reaction product and independently synthesized dineopentyl methylphosphonite coinjected and had identical mass spectra.

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The Synthesis and Absolute Configuration of Mycosporins. A Novel Application of the Staudinger Reaction

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The mycosporins, e.g., **1** and **2**, represent a structurally unique class of fungal metabolites[2] that are believed to exercise a regulatory effect on sporulation.[3] Although ubiquitous among both terrestrial and marine species,[4] mycosporins and their imino derivatives, e.g., **3** and **4**,[5] are notoriously unstable substances, suffering dehydration and consequent aromatization as well as hydrolysis to a meso cyclohexane-1,3-dione with facility. Further, in spite of the fact that mycosporins possess optical activity, their absolute configurations are unknown. We now report the first syntheses of **1** and **2** by a route that defines the configuration of the stereogenic centers in these two mycosporins as *S*. Our synthetic strategy illustrates a novel application of the Staudinger reaction[6] of an iminophosphorane for introducing the appropriate mycosporin side chain.

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