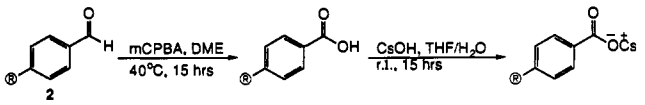
Scheme III



2

a 1:1.92 mixture of diastereomers in an 18% overall yield[11] from benzaldehyde. Attention was next turned to the polymer-supported version of this reaction protocol.

Commercially available 2%-cross-linked Merrifield polymer was oxidized to aldehyde[12] **2b** and condensed with nitromethane to form polymer-bound 2-nitro-1-phenylethan-1-ol **3b**. The hydroxyl moiety was protected as the trimethylsilyl ether **4b** in order to avoid dehydration to the corresponding β-nitrostyrene. Subsequent phenyl isocyanate mediated dehydration[13] of the nitroalkane moiety presumably generated the polymer-bound nitrile oxide, which then underwent 1,3-dipolar cycloaddition with 1,5-hexadiene (2–3-fold excess) to give the polymer-bound isoxazole **5b**. After each step in this sequence, polymer characterization was accomplished by comparing the IR spectrum[14] of the functionalized polymer with that of the solution-phase analog. Finally, electrophilic cyclization of the isoxazole with iodine monochloride at −78 °C gave **1** and regenerated the polymer-bound aldehyde. Using 3 equiv of 1,5-hexadiene, the overall yield was 0.26 mmol of **1**/g of polymer. The overall yield using 2 equiv of 1,5-hexadiene was 0.19 mmol of **1**/g of polymer. When the polymer-bound aldehyde was recycled through this reaction scheme, **1** was obtained to the extent of 0.07–0.11 mmol/g of polymer. In parallel with the solution-phase chemistry, the cis:trans ratio for **1** was 1:2.1.

A determination of the degree of functionalization of the polymer at the aldehyde stage was carried out in order both to accurately estimate the number of equivalents of α,ω-diene used and to assess the overall chemical yield of **1**.

Oxidation of the aldehyde **2** to a carboxylic acid (*m*-CPBA) followed by neutralization with cesium hydroxide and gravimetric analysis showed the degree of functionalization to be 0.65 ± 0.04 mequiv of aldehyde/g of polymer[15] (Scheme III). With this value as a basis, the overall yield of the 2-(cyanomethyl)-5-(iodomethyl)tetrahydrofuran from the polymer-bound aldehyde **2b** was calculated to be 40% using 3 equiv of 1,5-hexadiene and 29% using 2 equiv of 1,5-hexadiene. These yields were considerably higher than those of the solution-phase synthesis. When recovered polymer-bound aldehyde was recycled through the sequence, the overall yield of **1** was 11–17%.

We have shown that polymer-supported, multistep synthetic sequences can deliver small molecule targets. The diversity of reactions, solvents, and conditions presented in this five-step sequence demonstrates the versatility of the polymer-supported methodology. Reaction conditions are only slightly, if at all, different from those used in conventional synthesis, and it is also significant that the desired cyclic ether is formed exclusively; no other products are cleaved from the polymer support. In addition, the polymer support is sufficiently robust to be recovered and recycled through the reaction sequence.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9108231) and the Petroleum Research Fund of the American Chemical Society for the financial support of this research. Additional support was obtained for X.B. from the U.C. Davis Research Mentorship Program as well as the Graduate Research Award Program.

Supplementary Material Available: Detailed descriptions of synthesis and characterization of both solution-phase and polymer-supported reactions, including relevant FTIR, NMR, and elemental analysis data (3 pages). Ordering information is given on any current masthead page.

(11) Typical yield for a single run through the complete sequence. Using individually optimized yields for each step, an idealized overall yield of 29% is calculated.

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(15) These data are in agreement with IR and quantification results cited in ref 14.

Biosynthesis of Azoxy Compounds. Investigations of Valanimycin Biosynthesis†

Ronald J. Parry,* Yan Li, and Fwu-Lin Lii

Department of Chemistry, Rice University
P.O. Box 1892, Houston, Texas 77251

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The antibiotic valanimycin (**1**) is a naturally occurring azoxy compound produced by *Streptomyces viridifaciens* MG456-hF10. In addition to antibacterial activity, valanimycin exhibits potent antitumor activity against L1210 and P388 mouse leukemia cells.[1] As a naturally occurring azoxy compound, valanimycin is a member of a growing class of natural products which now includes the cycad toxins macrozamin and cycasin,[2-5] the carcinogen elaiomycin (**2**),[6-10] the antifungal agents LL-BH872α[11-13] and maniwamycins A and B,[14] and the nematocidal compounds jietacins A and B.[15]

Investigations of elaiomycin biosynthesis previously carried out in our laboratory revealed that the β-nitrogen atom and C-5–C-12 of **2** are derived from *n*-octylamine.[16] Additional investigations showed that the α-nitrogen atom and C-2–C-4 of **2** are derived from L-serine, while C-1 is derived from C-2 of acetate.[17] Further studies of elaiomycin were precluded due to insurmountable microbiological difficulties. We have therefore begun to examine the biosynthesis of valanimycin in a continuing effort to understand the biosynthesis of azoxy compounds and the mechanism of N–N bond formation. We would now like to summarize the results of our initial studies.

† This paper is dedicated to the memory of Edward Leete (1928–1992), a pioneer in the field of biosynthetic investigations.

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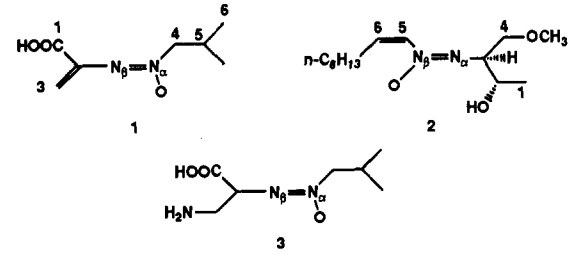

1 2

3

A preliminary examination of valanimycin biosynthesis has been carried out by Yamato et al.[18] These investigators showed that radioactive valine is incorporated primarily into the isobutyl moiety of the antibiotic, while radioactive alanine labels both the dehydroalanyl and isobutyl moieties of valanimycin. We have employed precursors labeled with stable isotopes in order to obtain more precise information concerning valanimycin biosynthesis. Since valanimycin is unstable, the antibiotic produced in these experiments was isolated as the stable ammonia adduct **3**.[1] The role of alanine in valanimycin biosynthesis was first examined by administration of [1-^{13}C]-, [2-^{13}C]-, and [3-^{13}C]-DL-alanine to *S. viridifaciens* fermentations. The ammonia adduct **3** isolated from these experiments exhibited low levels of enrichment at the expected positions of the valanimycin skeleton (C-1–C-3) (Table I, expts 1–3). In addition, the valanimycin derived from [2-^{13}C]- and [3-^{13}C]-DL-alanine exhibited a labeling pattern in the isobutyl moiety that is consistent with the conversion of alanine into valine via pyruvate and α-acetolactate.[19] These observations explain the incorporation of radioactivity from [U-^{14}C]-L-alanine into the isobutyl moiety reported by Yamato et al.[18]

Although the data from these three experiments can be clearly interpreted, the fact that the levels of enrichment observed for incorporation of alanine into the dehydroalanyl unit of **1** were quite low and that the labels from [2-^{13}C]- and [3-^{13}C]-alanine were more efficiently incorporated into the isobutyl moiety than into the dehydroalanyl moiety was somewhat surprising. These results suggested that alanine is metabolized very rapidly by growing cultures of *S. viridifaciens*. We therefore decided to examine the incorporation of alanine into valanimycin by washed cells[18] of this organism. Administration of [1-^{13}C]-DL-alanine to washed cells yielded valanimycin in which the specific enrichment in the dehydroalanyl moiety increased more than 20-fold (Table I, expt 4). Similarly, administration of [3-^{13}C]-DL-alanine to washed cells led to a dramatic increase in the incorporation of label into C-3 of **3** relative to that observed in nonresting cells (Table I, expt 5). This observation set the stage for an investigation of the origin of the β-nitrogen atom of valanimycin.

[2-^{13}C,^{15}N]-DL-Alanine was synthesized by reduction of sodium [2-^{13}C]pyruvate with sodium cyanoborohydride in the presence of [^{15}N]ammonium ions and administered to washed cells of *S. viridifaciens*. The ammonia adduct **3** isolated in this experiment exhibited strong ^{13}C enrichment at C-2, but no coupling of the ^{13}C label to ^{15}N could be observed (Table I, expt 6).[20] This result was unexpected since the two nitrogen atoms of elaiomycin have been shown to originate from the amine and amino acid building blocks for this antibiotic.[16,17] It appeared that a possible explanation for this contradiction might be an alternative origin for the dehydroalanine moiety of valanimycin. Since the dehydroalanine units of berninamycin and nosiheptide have been shown to originate from serine,[21-23] the role of this amino acid in valanimycin biosynthesis was examined. Administration of ^{13}C-labeled forms of serine to nonresting cells of *S. viridifaciens* gave very low incorporations into **3** (data not shown). On the other hand, administration of [1-^{13}C]- and [3-^{13}C]-DL-serine to washed cells yielded antibiotic that exhibited spectacularly high enrichments at C-1 and C-3 of the antibiotic (Table I, expt 7 and 8). An even more gratifying result was obtained by administration of [2-^{13}C,^{15}N]-DL-serine[17] to washed cells. In this instance, clear evidence was obtained for the incorporation of the serine nitrogen atom into the β-nitrogen atom of valanimycin (Table I, expt 9). It therefore appears that serine is a more direct precursor of the dehydroalanine moiety of valanimycin than is alanine.[24]

Table I. Incorporation of Precursors into Valanimycin

expt no.	precursor	% enrichment (labeling pattern)
1	[1-^{13}C]-DL-alanine	0.4 (C-1)
2	[2-^{13}C]-DL-alanine	0.2 (C-2)
		0.6 (C-4)
		0.4 (C-5)
3	[3-^{13}C]-DL-alanine	0.3 (C-3)
		1.1 (C-6)
4	[1-^{13}C]-DL-alanine[a]	8.5 (C-1)
5	[3-^{13}C]-DL-alanine[a]	23.5 (C-3)
		2.1 (C-6)
6	[2-^{13}C,^{15}N]-DL-alanine[a]	6.2 (C-2)
		0.5 (C-4)
		1.2 (C-4, J_{CC} = 34 Hz)
		0.7 (C-5)
		1.2 (C-5, J_{CC} = 34 Hz)
7	[1-^{13}C]-DL-serine[a]	96 (C-1)
8	[3-^{13}C]-DL-serine[a]	77 (C-3)
9	[2-^{13}C,^{15}N]-DL-serine[a]	83 (C-2, J_{CN} = 2.3 Hz)
10	[1-^{13}C]isobutylamine	8.7 (C-4)
11	[1-^{13}C,^{15}N]isobutylamine	8.6 (C-4, J_{CN} = 9.3 Hz)
12	[1-^{13}C]isobutylhydroxylamine	50 (C-4)
13	[1-^{13}C,^{15}N]isobutylhydroxylamine	48 (C-4, J_{CN} = 9.3 Hz)

[a] Experiment using washed cells.

On the basis of the analogy provided by elaiomycin biosynthesis, it appeared likely that the remaining portion of the valanimycin skeleton might be derived from isobutylamine. This hypothesis was first evaluated by means of a precursor incorporation experiment with [1-^{13}C]isobutylamine, which was synthesized in two steps from 2-bromopropane by treatment with potassium [^{13}C]-cyanide in HMPA[25] followed by catalytic reduction of the resulting [1-^{13}C]isobutyronitrile. The results of this experiment clearly demonstrate that isobutylamine is an efficient and specific precursor of valanimycin (Table I, expt 10). The origin of the α-nitrogen atom of valanimycin was then examined by administration of [1-^{13}C,^{15}N]isobutylamine synthesized from potassium [^{13}C,^{15}N]cyanide. The ammonia adduct isolated from this fermentation clearly exhibited ^{15}N–^{13}C coupling, thereby demonstrating that the α-nitrogen atom of valanimycin is indeed derived from isobutylamine (Table I, expt 11). The biosynthesis of valanimycin therefore follows the pattern first observed with elaiomycin.[16,17]

A major question to be addressed with respect to the biosynthesis of naturally occurring azoxy compounds is the mechanism of formation of the N–N bond. This question is of general interest since compound containing N–N linkages are widespread among natural products.[26] At present, relatively little appears to be known about N–N bond formation, but a potential clue to the mechanism is provided by the fact that some soil microorganisms can catalyze the formation of azobenzene derivatives from substituted anilines. These reactions appear to involve peroxidases, and the intermediacy of an aryl hydroxylamine has been sug-

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(24) Although serine is obviously a much more efficient precursor of valanimycin than is alanine, the fact remains that all three carbons of alanine are specifically incorporated into the expected positions of valanimycin. Since the conversion of alanine into serine has not been reported to occur in living systems, the mechanism for the observed incorporation of alanine into valanimycin is unclear at the present time.

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gested.[27] The aryl hydroxylamine is postulated to react with unoxidized aryl amine to generate a hydrazo compound that is then oxidized to the azo derivative.[27] This information suggested that isobutylhydroxylamine might be an intermediate in valanimycin biosynthesis. Accordingly, [1-^{13}C]isobutylhydroxylamine was synthesized from [1-^{13}C]isobutylamine by a modification of the methodology of Polonski and Chimiak[28] and administered to *S. viridifaciens*. To our satisfaction, the resulting valanimycin exhibited a ^{13}C enrichment which was about 6 times higher than that obtained with isobutylamine (Table I, expt 12). Additional proof for the intact incorporation of isobutylhydroxylamine into valanimycin was obtained by administration of [1-^{13}C,^{15}N]isobutylhydroxylamine, which was synthesized from [1-^{13}C,^{15}N]-isobutylamine. The valanimycin ammonia adduct isolated from this experiment exhibited high enrichment as well as the anticipated ^{13}C–^{15}N coupling (Table I, expt 13). The findings from these two experiments supply the first evidence for the intermediacy of a hydroxylamine in the biosynthesis of an aliphatic azoxy compound, and they provide support for the hypothesis that N–N bond formation involves the reaction of a hydroxylamine with an amine.[29]

Acknowledgment. We thank Dr. Tomio Takeuchi for a culture of *Streptomyces viridifaciens* and the National Institutes of Health (Grant CA-25142) and The Robert A. Welch Foundation (Grant C-729) for financial support.

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Phosphorus Analogue (C≡P$^-$) of a Bridging Cyanide (C≡N$^-$) Ligand: Synthesis and Structure of (Cl)(PEt$_3$)$_2$Pt(μ-C≡P)Pt(PEt$_3$)$_2$

Hyoung Jun, Victor G. Young, Jr.,† and Robert J. Angelici*

Department of Chemistry, Iowa State University
Ames, Iowa 50011-3111

Received August 10, 1992

The cyanide ion (C≡N$^-$) is a common ligand in transition metal complexes.[1] It coordinates through the carbon at single metal centers (A, Chart I) or bridges two metals as in B,[2a] C,[2b] or D[2c] in Chart I. To our knowledge, the phosphorus analogue (C≡P$^-$) of the C≡N$^-$ ligand is unknown.[2d] In this communication, we report the synthesis and structure of the first example of a complex containing the cyaphide[3] (C≡P$^-$) ligand. In this complex, (Cl)(PEt$_3$)$_2$Pt(μ-C≡P)Pt(PEt$_3$)$_2$, the C≡P$^-$ ligand bridges the two Pt atoms in a manner not found in any of the known C≡N$^-$-bridged structures (B, C, or D).

The complex is prepared as outlined in Scheme I. In 20 mL of benzene, **1**[4] (0.395 g, 0.500 mmol) reacts with equimolar Pd(PEt$_3$)$_4$[5] (0.289 g, 0.500 mmol) at room temperature for 8 h under Ar to give only two products, **2**[6] and **3**,[7] as established by ^{31}P NMR studies of the mixture. Complex **2** is isolated in 86% yield as air-stable, colorless crystals by evaporating the reaction solution to dryness and recrystallizing the residue from hexanes at −78 °C; under these conditions **3** partially decomposes to unidentified materials. However, when equimolar Pt(PEt$_3$)$_4$ (0.334 g, 0.500 mmol) in 5 mL of benzene is added to the reaction mixture of **2** and **3** and the solution is stirred at room temperature under Ar for 30 min, moderately air-stable, light brown crystals of **4**[8] are isolated in an overall 80% yield (based on **1**) by evaporating the reaction solution to dryness and recrystallizing the residue from hexanes at −78 °C. Under these conditions, **4** precipitates after **2**.

The structure of **4**, as established by a single-crystal X-ray diffraction study,[9] shows that it contains a bridging C≡P$^-$ ligand

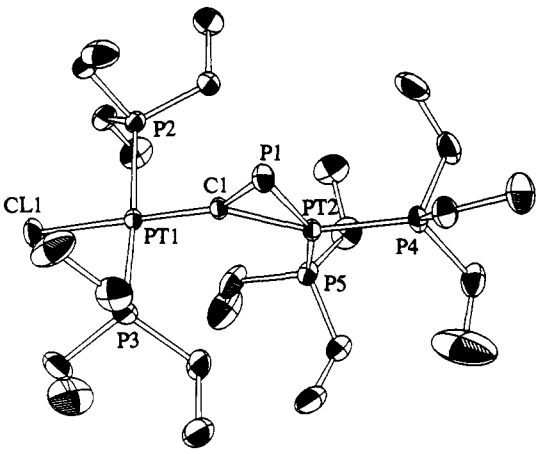
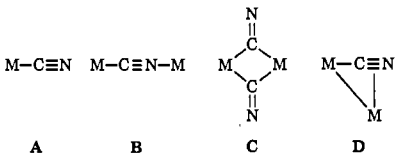
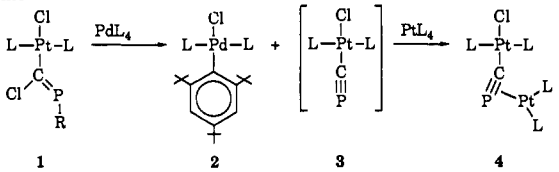


Figure 1. ORTEP drawing of (Cl)(PEt$_3$)$_2$Pt(μ-C≡P)Pt(PEt$_3$)$_2$ (**4**). Selected bond distances (Å) and angles (deg) are C(1)–P(1) = 1.666 (6), Pt(1)–C(1) = 1.950 (6), Pt(2)–C(1) = 2.083 (5), Pt(2)–P(1) = 2.337 (2), Pt(2)–P(4), = 2.269 (2), Pt(2)–P(5) = 2.277 (2), Pt(1)–C(1)–P(1) = 144.0 (3), Pt(1)–C(1)–Pt(2) = 139.7 (3), C(1)–Pt(2)–P(1) = 43.8 (2), P(4)–Pt(2)–P(5) = 104.20 (6).

Chart I



Scheme I



R = 2,4,6-tri-tert-butylphenyl
L = PEt$_3$

† Iowa State University, Molecular Structure Laboratory.

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(6) **2**: ^{1}H NMR (C$_6$D$_6$) δ 7.42 (t, 2 H, J_{PH} = 0.97 Hz, R), 1.89 (s, 18 H, CH$_3$ of R), 1.68 (t, q, 12 H, J_{HH} = 7.08 Hz, J_{PH} = 2.69 Hz, CH$_2$ of Et), 1.34 (s, 9 H, CH$_3$ of R), 0.88 (5 lines; 18 H, J_{HH} = 7.08 Hz, CH$_3$ of Et); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 85% H$_3$PO$_4$ external standard) δ −2.75 (s, PEt$_3$). Anal. Calcd for C$_{30}$H$_{59}$ClP$_2$Pd: C, 57.83; H, 9.47. Found: C, 57.60; H, 9.56.
(7) **3**: ^{31}P{^{1}H} NMR (C$_6$D$_6$, 85% H$_3$PO$_4$ external standard) δ 68.0 (t, J_{PP} = 9.16 Hz, J_{PtP} = 303 Hz from ^{195}Pt satellites, C≡P), 7.3 (d, J_{PP} = 9.16 Hz, J_{PtP} = 2871 Hz, PEt$_3$).
(8) **4**: ^{31}P{^{1}H} NMR (C$_6$D$_6$, 85% H$_3$PO$_4$ external standard) δ 107.0 (t, d, d, $^3J_{P_1P_2}$ = 10.68 Hz, $^2J_{P_1P_4}$ = 10.68 Hz, $^2J_{P_1P_5}$ = 13.73 Hz, $^1J_{Pt_2P_1}$ = 58 Hz, $^2J_{Pt_1P_1}$ = 255 Hz, C≡P$_1$), 18.6 (d, d, $^2J_{P_1P_4}$ = 10.68, $^2J_{P_4P_5}$ = 35.10 Hz, $^1J_{Pt_2P_4}$ = 3619 Hz, $^3J_{Pt_1P_4}$ = 137 Hz, P$_4$), 15.0 (t, d, d, $^4J_{P_5P_2}$ = 4.52 Hz, $^2J_{P_5P_4}$ = 35.10, $^2J_{P_5P_1}$ = 13.73 Hz, $^1J_{Pt_2P_5}$ = 3155 Hz, P$_5$), 4.9 (d, d, $^3J_{P_2P_1}$ = 10.68 Hz, $^4J_{P_2P_5}$ = 4.52 Hz, $^1J_{Pt_1P_2}$ = 2936 Hz, P$_2$, P$_3$). Anal. Calcd for C$_{25}$H$_{60}$ClP$_5$Pt$_2$: C, 31.89; H, 6.38. Found: C, 31.72; H, 6.61.

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