(2 C), 18.61 (t), 18.47 (t), 13.79 (q) (4 C); IR (liquid film) 3400, 2970, 2940, 2880, 1470, 1460, 1380, 1130, 1075, 1030 cm^{-1}.

(5*E*,9*E*)- and (5*Z*,9*E*)-Octahydro-3-*n*-butyl-5-*n*-propylindolizin-7-ol (2 and 7). Freshly distilled $MeSO_2Cl$ (0.45 mL, 669 mg, 5.8 mmol) was added dropwise to a solution of the alcohols **6a,b** (746 mg, 2.9 mmol) in 7.5 mL of anhydrous pyridine, cooled to −10 °C. After 4 h of being stirred at the same temperature, the reaction mixture was poured in ice and extracted with CH_2Cl_2 (four times, 15 mL). The combined organic layers were washed with 1 N aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated to yield the methanesulfonate derivatives quantitatively. The crude oil was dissolved in MeOH (10 mL), added with 26 mg of 10% Pd on C, and hydrogenated under atmospheric pressure of hydrogen. After 57 h the reaction, monitored by TLC, was completed. After filtration on Celite, the methanolic solution was treated with 1 N aqueous NaOH (3 mL), and the mixture was stirred for 2 h. The solution was then concentrated, and the yellow residue was dissolved in CH_2Cl_2 (20 mL) and washed twice with H_2O. The organic layer was dried (Na_2SO_4) and concentrated, and the oil obtained was chromatographed on a short pad of silica gel by eluting in sequence with CH_2Cl_2, EtOAc, and MeOH. The more polar fractions contained a 1.4:1 mixture of the indolizidinols **2** and **7** (471 mg, 67%). The two isomers can be separated by flash chromatography (El, ethyl acetate): **7**, R_f = 0.35; **2**, R_f = 0.25. Anal. Calcd for $C_{15}H_{29}NO$: C, 75.26; H, 12.21; N, 5.85. Found: C, 75.10; H, 12.08; N, 6.11.

2 (5*E*,9*E*): MS *m/z* (relative intensity) 239 ($2^{\bullet+}$, 1), 238 (1), 196 (91, loss propyl), 182 (100, loss butyl), 152 (17), 41 (9); ^1H NMR δ 3.61 (br s, 1 H), 3.55 (m, 1 H), 3.27 (m, 1 H), 2.51 (m, 1 H), 2.12–1.81 (m, 3 H), 1.65–1.05 (m, 16 H), 0.88 (t, J = 7.2 Hz, 3 H), 0.86 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 69.20 (d), 57.80 (d), 57.44 (d), 53.77 (d), 40.85 (t), 39.64 (t), 35.17 (t), 28.99 (t), 28.76 (t), 26.77 (t), 25.43 (t), 22.71 (t), 18.65 (t), 13.80 (q), 13.74 (q); IR (CCl_4) 3621, 3364 (broad), 2959, 2931, 2873, 2860, 2801 and 2680 (Bohlmann's bands), 1464, 1380, 1184, 1117, 1094, 1012 cm^{-1}.

7 (5*Z*,9*E*): MS *m/z* (relative intensity) 239 ($7^{\bullet+}$, 2.7), 238 (2.1), 196 (100, loss propyl), 182 (98, loss butyl), 152 (23), 41 (16); ^1H NMR δ 3.82 (m, 1 H), 3.25 (m, 1 H), 2.98 (m, 1 H), 2.80 (m, 1 H), 2.08–1.85 (m, 2 H), 1.65–1.0 (m, 17 H), 0.87 (m, 6 H); ^{13}C NMR δ 65.22 (d), 58.75 (d), 54.96 (d), 53.34 (d), 36.60 (t), 35.56 (t), 35.17 (t), 31.95 (t), 28.99 (t), 28.33 (t), 28.17 (t), 22.87 (t), 20.25 (t), 14.01 (q), 13.90 (q); IR (CCl_4) 3617, 3345 (broad), 2959, 2931, 2872, 2860, 1467, 1378, 1144, 1192, 1101, 1019 cm^{-1}.

(5*E*,9*E*)- and (5*Z*,9*E*)-Octahydro-3-*n*-butyl-5-*n*-propylindolizin-7-ol *S*-Methyl Dithiocarbonate (8 and 9). A mixture of 120 mg (5.0 mmol) of sodium hydride, 756 mg (3.16 mmol) of the alcohols **2** and **7**, 21 mg (0.316 mmol) of imidazole, and 20 mL of dry tetrahydrofuran was heated to reflux for 3 h, followed by the addition of 1 mL (17.0 mmol) of carbon disulfide. The mixture was warmed under reflux for 30 min, and 1 mL (17.0 mmol) of methyl iodide was added. The mixture was warmed for 30 min longer and then partitioned between 50 mL of CH_2Cl_2 and 50 mL of water. The aqueous phase was extracted twice with 20 mL of CH_2Cl_2, and the combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The oil residue was flash chromatographed (El, EtOAc 15% in petroleum ether) to give two fractions: R_f = 0.6, 409 mg (mixture of isomers **9** and **8** in 9:1 ratio, yield 39%), and R_f = 0.4, 468 mg (pure **8**, yield 45%). **8** (Anal. Calcd for $C_{17}H_{31}NOS_2$: C, 61.95; H, 9.48; N, 4.25. Found: C, 61.82; H, 9.69; N, 3.96): MS *m/z* (relative intensity) 329 ($8^{\bullet+}$, 0.9), 286 (37), 272 (100), 222 (48), 178 (88), 164 (16), 126 (14), 122 (11), 55 (16), 41 (13); ^1H NMR δ 5.48 (tt, J = 11.4, 4.5 Hz, 1 H), 3.24 (br t, J = 9 Hz, 1 H), 2.59 (m, 1 H), 2.51 (s, 3 H), 2.27 (m, 2H), 1.92 (m, 2H), 1.69–0.95 (m, 15 H), 0.91 (t, J = 6.9 Hz, 3 H), 0.89 (t, J = 7.5 Hz, 3 H); ^{13}C NMR δ 214.96, 81.59, 57.52, 56.49, 53.13, 36.80, 35.44, 35.33, 29.22, 28.84, 26.82, 25.22, 22.72, 18.56, 18.46, 14.22, 13.96; IR (CCl_4) 2960, 2930, 2880, 2860, 2810, 1220, 1050 cm^{-1}. **9**: ^1H NMR δ 5.78 (tt, J = 9.0, 3.4 Hz, 1 H), 3.37 (m, 1 H), 3.05 (m, 1 H), 2.87 (m, 1 H), 2.53 (s, 3 H), 2.09–1.88 (m, 2 H), 1.88–1.03 (m, 16 H), 0.92 (m, 6 H); ^{13}C NMR δ 214.78, 80.00, 57.93, 54.12, 53.12, 35.85, 35.56, 32.52, 29.09, 28.14, 27.54, 22.93, 20.25, 20.19, 18.62, 18.56, 13.90 (2 C).

(5*E*,9*E*)-Octahydro-3-*n*-butyl-5-*n*-propylindolizine (1). A solution of the xanthate **8** (110 mg, 0.33 mmol) in dry toluene (5 mL) was added dropwise to a boiling mixture of tributyltin hydride (0.135 mL, 146 mg, 0.50 mmol) and azoisobutyronitrile (catalytic) in the same solvent (5 mL). The resulting solution was warmed under reflux for additional 5 h and then concentrated in vacuo. The residue was chromatographed over silica gel, eluting first with petroleum ether and then with 15% ethyl acetate in petroleum ether. Eventually **1** was eluted from the column with 9:1 ethyl acetate–triethylamine: 59 mg (79%); volatile pale yellow oil; MS *m/z* (relative intensity) 223 ($1^{\bullet+}$, 1), 222 (2), 181 (11), 180 (88), 167 (12), 166 (100), 164 (2), 124 (13), 122 (9), 81 (6), 55 (11), 41 (20); ^1H NMR δ 3.29 (m, 1 H), 2.38 (m, 2 H), 1.95–0.97 (m, 20), 0.91 (t, J = 7 Hz, 3 H), 0.89 (t, J = 7 Hz, 3 H); ^{13}C NMR δ 58.90 (d), 58.39 (d), 56.50 (d), 35.77 (t), 32.26 (t), 30.84 (t), 29.94 (t), 29.01 (t), 26.25 (t), 24.86 (t), 24.56 (t), 22.83 (t), 18.85 (t), 14.39 (q), 14.03 (q); IR ($CDCl_3$) 2970, 2940, 2880, 2860, 2810 cm^{-1}.

(5*Z*,9*E*)-Octahydro-3-*n*-butyl-5-*n*-propylindolizine (10). The above procedure was repeated on the epimer **9**; with eluent ethyl acetate, **10** was isolated as a volatile pale yellow oil, yield 38%: MS *m/z* (relative intensity) 223 ($10^{\bullet+}$, 2), 222 (3), 181 (13), 180 (100), 166 (95), 124 (13), 55 (9), 41 (15); ^1H NMR δ 3.07 (m, 1 H), 2.55 (m, 1 H), 2.44 (m, 1 H), 1.87–1.04 (m, 20 H), 0.90 (m, 6 H); ^{13}C NMR δ 58.42 (d), 56.09 (d), 52.38 (d), 32.28 (t), 29.29 (t), 28.63 (t), 28.54 (t), 28.16 (t), 27.62 (t), 22.95 (t), 22.80 (t), 20.67 (t), 19.20 (t), 14.35 (q), 13.96 (q).

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Registry No. (±)-**1**, 81076-50-8; (±)-**2**, 118798-53-1; (±)-**3**, 118798-54-2; **4**, 628-05-7; (±)-**5**, 118798-55-3; (±)-**6** (isomer 1), 118798-56-4; (±)-**6** (isomer 2), 118916-45-3; (±)-**7**, 118916-43-1; (±)-**8**, 118798-57-5; (±)-**9**, 118916-44-2; (±)-**10**, 81076-53-1; CH_2=CHCHO, 107-02-8; (±)-1-hepten-4-ol, 111321-98-3.

Synthesis of *O*-Phosphotyrosine-Containing Peptides. 1. Synthesis of *P*Tyr-Leu-Gly via Benzyl Phosphate Protection

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The recent recognition of tyrosine phosphorylation as an important step in several cellular processes[1-7] has necessitated the need for the development of a synthetic methodology suitable for the production of synthetic *P*Tyr peptides for use as model substrates. In contrast to the well-documented synthetic methodology outlined for the preparation of *P*Ser peptides,[8-11] the synthetic methodology for the preparation of *P*Tyr peptides is not as well developed and is limited to only two recent significant studies. In the first of these studies, Valerio et al.[12] prepared Leu-Arg-Arg-Ala-*P*Tyr-Leu-Gly in an overall yield

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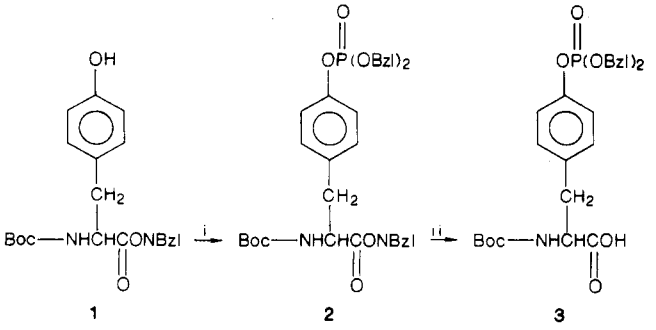
Scheme I[a]



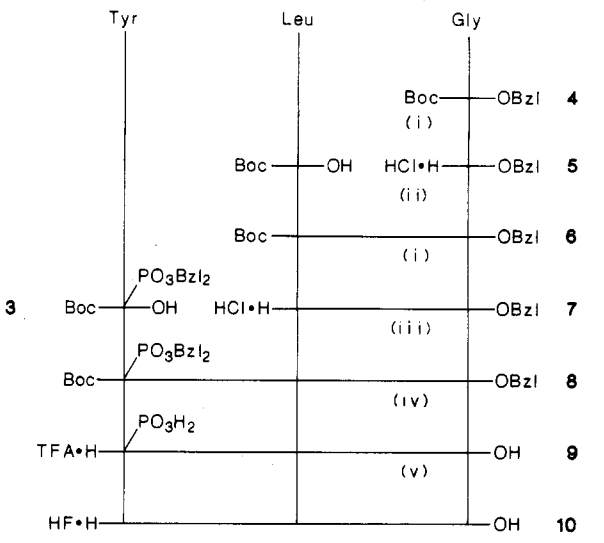
[a] (i) (a) $(BzlO)_2PNEt_2$/1*H*-tetrazole (15 min, 20 °C), then (b) MCPBA (−40 °C); (ii) $Na_2S_2O_4$ (pH 8.6, 1 h, 50 °C).

of 22% by the use of Boc-Tyr(PO_3Me_2)-OH in a Merrifield Boc/solid-phase peptide synthesis protocol and 33% HBr/AcOH for the acidolytic removal of the methyl phosphate groups. Later, Gibson et al.[13] prepared Val-*P*Tyr-Phe and Arg-*P*Tyr-Val-Phe in low yield by the use of Boc-Tyr(PO_3Bzl_2)-OH in a Yamashiro Boc/solid-phase peptide synthesis protocol and liquid hydrogen fluoride for final peptide deprotection.

This latter work has prompted us to bring to attention our previously unpublished studies regarding the application of Boc-Tyr(PO_3Bzl_2)-OH to peptide synthesis. In this paper, we report that peptide synthesis using Boc-Tyr(PO_3Bzl_2)-OH is limited due to (a) the marked sensitivity of benzyl phosphate groups under mild acidolytic conditions (40% TFA/CH_2Cl_2) used in peptide synthesis and (b) liquid hydrogen fluoride effects complete dephosphorylation of the *O*-phosphotyrosyl residue. Also, we describe the efficient Boc/solution-phase synthesis of the tripeptide H-*P*Tyr-Leu-Gly-OH TFA by the use of Boc-Tyr(PO_3Bzl_2)-OH in peptide synthesis and a final palladium-catalyzed hydrogenolytic deprotection step.

In an extension of our previous synthetic route,[12] Boc-Tyr(PO_3Bzl_2)-OH (**3**) was prepared by an efficient two-step procedure that featured the use of the efficient (i) $(BzlO)_2PNEt_2$/1*H*-tetrazole– (ii) MCPBA procedure[14] for the near-quantitative "phosphite-triester" phosphorylation[15] of Boc-Tyr-ONBzl (**1**) followed by sodium dithionite reduction[16] of the 4-nitrobenzyl ester from **2** (Scheme I). The structures of both Boc-amino acids **2** and **3** were confirmed by ^{13}C NMR spectroscopy and these data are consistent with ^{13}C NMR data previously obtained by Valerio.[17] The synthesis of Boc-Tyr(PO_3Bzl_2)-Leu-Gly-OBzl (**8**) was readily accomplished in 95% yield by the mixed anhydride condensation of Boc-Tyr(PO_3Bzl_2)-OH (**3**) with H-Leu-Gly-OBzl·HCl (**7**) (Scheme II). Successful incorporation of the -Tyr(PO_3Bzl_2)- residue into the peptide was established by its ^{13}C NMR spectrum, which displayed phosphorus-coupled doublet signals for the C3 (J_{PC} = 4.40 Hz) and C4 (J_{PC} = 7.33 Hz) aromatic carbons of the tyrosine residue. Subsequent palladium-catalyzed hydrogenolysis of tripeptide **8** in 50% CF_3CO_2H/CH_3CO_2H proceeded readily and gave H-Tyr(PO_3H_2)-Leu-Gly-OH·TFA (**9**) as a white solid in 99.5% yield. Structural confirmation of tripeptide **9** was readily established by fast atom bombardment mass spectrometry (FAB-MS), its positive and negative FAB mass spectra

Scheme II[a]



[a] (i) 4 M hydrogen chloride/dioxane (20 °C, 30 min); (ii) (a) NMM, IBCF (−20 °C, 3 min), then (b) amino acid **5** and NMM (1 equiv) in THF/DMF; (iii) (a) NMM, IBCF (−20 °C, 3 min), then (b) dipeptide **7** and NMM (1 equiv) in THF; (iv) H_2–10% Pd/C, 50% TFA/AcOH; (v) liquid hydrogen fluoride/anisole (9:1) (0 °C, 60 min).

displaying high intensity $[M]^+$ and $[M-2H]^-$ ions at m/z 432 and 430, respectively, and fragment ions resulting from initial cleavage of the phosphate group (PO_3H).

In the course of these studies, it was also observed that the *P*Tyr residue was unstable in liquid hydrogen fluoride, a 60-min treatment of H-*P*Tyr-Leu-Gly-OH·TFA with liquid hydrogen fluoride/anisole (9:1) at 0 °C effecting complete dephosphorylation and the recovery of H-Tyr-Leu-Gly-OH HF (**10**) in near-quantitative yield. The high sensitivity of the *P*Tyr residue under these conditions therefore precludes the use of liquid hydrogen fluoride for the general deprotection of protected Tyr(PO_3Bzl_2)-containing peptides. Moreover, since recent studies have shown that liquid hydrogen fluoride does not effect methyl phosphate cleavage but causes direct cleavage of the tyrosyl *O*-(dimethylphosphoro) group (the rate of cleavage varying under "low" and "high" hydrogen fluoride treatments),[18] it is clear that conventional liquid hydrogen fluoride procedures are unsuitable for the general preparation of *P*Tyr-containing peptides.

While tripeptide **9** was readily prepared in high yield, peptide extension of tripeptide **8** with Boc-Ala-OH using the mixed anhydride procedure did not proceed smoothly, the recovered residue being shown by ^{13}C and ^{31}P NMR spectroscopy to be Boc-Ala-Tyr($PO_3Bzl\{H\}$)-Leu-Gly-OBzl (**11**) in 22% yield. A ^{31}P NMR based study established that the low yield of the tetrapeptide was due to extensive acidolytic cleavage of the benzyl groups during removal of the Boc group from tripeptide **8** with 50% TFA/CH_2Cl_2, the rate of benzyl phosphate cleavage being considerably faster than that observed for the acidolytic debenzylation of Ser(PO_3Bzl_2) residues with 50% TFA/CH_2Cl_2 or 4 M HCl/dioxane.[8,19] In view of the acidolytic sensitivity of the benzyl phosphate groups under conventional Boc/peptide synthesis conditions, it is clear that Boc-Tyr-(PO_3Bzl_2)-OH is unsuitable for use in the synthesis of large Tyr(PO_3Bzl_2) peptides by either solution- or solid-phase methodologies.

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While the solution-phase synthesis of Leu-Arg-Arg-Ala-*P*Tyr-Leu-Gly using synthon **3** was not possible, the above study has demonstrated (a) that the dibenzyl *N,N*-diethylphosphoramidite phosphite-triester phosphorylation procedure is ideal for the phosphorylation of protected tyrosine derivatives, (b) that benzyl phosphate groups undergo rapid acidolytic debenzylation in 40–50% TFA/CH_2Cl_2, and (c) that liquid hydrogen fluoride effects quantitative dephosphorylation of *P*Tyr residues. Despite these two latter complications, we can nevertheless suggest the use of Boc-Tyr(PO_3Bzl_2)-OH as a suitable synthon in the synthesis of N-terminal *P*Tyr peptides providing that the final hydrogenolytic cleavage is not precluded by catalyst-poisoning amino acid residues (e.g., methionine or cystine). Alternatively, we can also recommend the dimethyl phosphate derivative, Boc-Tyr(PO_3Me_3)-OH, for use in Boc/solution- and Boc/solid-phase *P*Tyr peptide synthesis and that we have successfully used this derivative for the synthesis of large, complex *P*Tyr-containing peptides.[12,17,18]

Experimental Section

General Methods. The ^{13}C NMR spectra of Boc-amino acids **2** and **3** and tripeptide **8** were obtained as $CDCl_3$ solutions on a JEOL-FX 100 Fourier transform instrument operating at 25.00 MHz and referenced to internal tetramethylsilane. The ^{13}C NMR spectrum of tripeptide **9** was obtained as a D_2O solution and referenced to internal dioxane set to 66.5 ppm. The ^{31}P NMR spectra were obtained on a JEOL-FX 100 Fourier transform instrument operating at 40.26 MHz and referenced to external 85% H_3PO_4. The FAB mass spectra were obtained on a JEOL-DX 300 mass spectrometer equipped with a FAB source and used acetic acid/glycerol as matrix support. The optical rotation of tripeptides **8** and **9** were obtained as $CHCl_3$ or D_2O solutions, respectively, and were measured on a Perkin-Elmer 241 MC polarimeter with a 1-dm path length cell kept at constant temperature. Acetic acid and trifluoroacetic acid were of analytical reagent grade and used without purification.

Boc-Tyr(PO_3Bzl_2)-ONBzl (2). 1*H*-Tetrazole (1.16 g, 16.5 mmol) was added in one portion to a solution of Boc-Tyr-ONBzl (**1**) (2.08 g, 5.00 mmol) and dibenzyl *N,N*-diethylphosphoramidite (1.74 g, 5.50 mmol) in dry tetrahydrofuran (5 mL), and the resulting solution was then stirred for 15 min at 20 °C. The mixture was then cooled to −40 °C and a solution of 85% *m*-chloroperoxybenzoic acid (1.22 g, 6.00 mmol) in dichloromethane (12 mL) was added such that the temperature of the solution was maintained below 0 °C. After stirring for 10 min at 20 °C, 10% $Na_2S_2O_5$ (25 mL) and diethyl ether (100 mL) were added, the aqueous phase was discarded, and the ethereal phase was washed with 10% $Na_2S_2O_5$ (1 × 50 mL), 5% $NaHCO_3$ (1 × 50 mL), and 1 M HCl (1 × 50 mL), dried (Na_2SO_4), and filtered. The solvent was then removed by evaporation under reduced pressure and the light yellow oil then triturated with hexane (3 × 50 mL). On prolonged standing, the light yellow oil (3.24 g, 96%) became an off-white solid, mp 81–82 °C (lit.[13] mp 81–82 °C).

Boc-Tyr(PO_3Bzl_2)-OH (3). Sodium dithionite reduction[16] of **2** (3.04 g, 4.50 mmol) was performed according to previously described procedures[13,20] and gave **3** as a light yellow oil (1.87 g, 77%), which became a white solid on standing, mp 91–92.5 °C (lit.[13] mp 91.5–92.5 °C).

Boc-Tyr(PO_3Bzl_2)-Leu-Gly-OBzl (8). *N*-Methylmorpholine (0.28 g, 2.80 mmol) in THF (1 mL) and isobutyl chloroformate (0.355 g, 2.60 mmol) in THF (1 mL) were successively added to a solution of Boc-Tyr(PO_3Bzl_2)-OH (1.52 g, 2.80 mmol) in THF (10 mL) at −20 °C. After an activation period of 3 min, a solution of dipeptide **7** (0.63 g, 2.00 mmol) and *N*-methylmorpholine (0.20 g, 2.00 mmol) in THF (4 mL) was added, and the resulting solution was stirred for 2 h at −20 °C prior to the addition of 5% $NaHCO_3$ (5 mL). After 30 min at 20 °C, dichloromethane (100 mL) was added and the organic phase washed with 5% $NaHCO_3$ (2 × 30 mL) and 1 M HCl (2 × 30 mL), dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure gave tripeptide **8** as a light brown oil (1.52 g, 95%): $[\alpha]^{23}_D$ −18.0° (*c* 1, $CHCl_3$); ^1H NMR ($CHCl_3$) δ 0.75–1.02 (m, 6 H, Leu CH_3), 1.42 (s, 9 H, Boc CH_3), 1.50–1.72 (b m, 3 H, Leu γ-CH and Leu β-CH_2), 2.00–2.40 (b m), 2.9–3.2 (b m), 3.9–4.1 (b m), 5.10 and 5.13 (each d, 2 H, J_{PO-CH} = 8.35 Hz, PO_3Bzl_2), 5.18 (s, 2 H, Bzl CH_2), 6.4 and 6.7 (each b d, 1 H, Tyr(PO_3Bzl_2) and Leu NH), 6.9–7.2 (b dd, Tyr ArH), 7.2–7.4 (m, 15 H, Bzl ArH); ^{13}C NMR ($CHCl_3$) δ 21.77, 22.65, 24.35, 28.03, 37.16, 40.79, 41.02, 51.43, 55.53, 66.88, 69.83 (d, *J* = 4.39 Hz), 80.04, 119.80 (d, *J* = 4.40 Hz), 127.84, 128.13, 128.42, 130.53, 135.10 (d, *J* = 5.86 Hz), 149.44 (d, *J* = 7.33 Hz), 155.57, 169.38, 171.60, 171.89, 172.36; ^{31}P NMR ($CHCl_3$) δ −6.4.

H-Tyr(PO_3H_2)-Leu-Gly-OH TFA (9). A solution of tripeptide **8** (0.80 g, 1.00 mmol) in 50% TFA/AcOH (4 mL) containing 10% palladium on charcoal (0.30 g) was charged with hydrogen at atmospheric pressure. On cessation of hydrogen uptake 30 min), the catalyst was removed by gravity filtration and the solvent removed under reduced pressure. Repeated trituration of the residue with diethyl ether (3 × 30 mL) followed by high vacuum drying gave tripeptide **9** as a white solid (0.542 g, 99.5%), mp 172–175 dec: $[\alpha]^{23}_D$ −8.30° (*c* 1, H_2O); ^{13}C NMR (D_2O) δ 21.01, 21.84, 24.08, 35.98, 39.93, 41.00, 52.26, 54.02, 120.84 (d, *J* = 4.40 Hz), 129.06, 130.62, 151.56 (d, *J* = 7.69 Hz), 168.65, 172.74, 173.86; ^{31}P NMR (D_2O) δ −3.8; FAB mass spectrum (Ar, positive mode), *m/z* (rel intensity) 454 ($[M - H + Na]^+$, 1), 432 ($[M]^+$, 16), 416 (1), 352 ($[M - PO_3H]^+$, 9), 336 ($[M - 96]^+$, 1), 329 (3), 245 (4.5), 227 (2.5), 216 (9), 207 (5), 189 (9), 136 (23), 115 (23), 86 (100); FAB mass spectrum (Ar, negative mode), *m/z* (rel intensity) 430 ($[M - 2H]^-$, 57), 415 (7), 372 (4), 350 ($[M - 2H - PO_3H]^-$, 9), 335 (4), 297 (4), 259 (6), 243 (4), 214 (6), 165 (8), 151 (16), 127 (8), 97 (23), 80 (100).

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Generation and Rearrangement of Unsaturated Hydrocarbons from Flash Vacuum Pyrolysis of Dichlorocyclopropanes at 850 °C

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Although the gas-phase, thermal rearrangements of dihalocyclopropanes to halodienes and to trienes have been observed to occur at temperatures <700 °C,[1-6] only in the

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