in tomaymycin, the biosynthetic pathway leading to PD 125375 is obscure.

Experimental Section

General Methods. ^{13}C and ^{1}H data were obtained at 75.4 and 300 MHz, respectively, on a Varian XL-300 NMR spectrometer. Quadrature mode detection was used for all NMR experiments. Data processing was performed with the Motorola VM02-based data system. COSY and NOESY spectra were obtained by recording a data matrix of 256 × 256 complex points. A spectral width of 1774.0 Hz was used in both domains. An incremented mixing period was used in the NOESY experiment to reduce the intensity of J-correlated cross peaks.[7] Pseudo-echo weighting was performed along both dimensions prior to Fourier transformation. The 2D data were symmetrized to remove false peaks. HETCOR spectra were obtained by recording a data matrix of 64 × 1024 complex points. Spectral widths of 1774.0 Hz and 11351.0 Hz were used along the t_1 (^{1}H) domain and the t_2 (^{13}C) domain, respectively. Exponentional broadening was applied along both dimensions. Prior to Fourier transformation the t_1 and t_2 domains were zero-filled to 128 points and 2048 points, respectively. All spectra were converted to an absolute value mode and then a contour-type plot was made. Carbon multiplicities were determined by performing a DEPTGL[8] experiment. The optical rotation of PD 125375 was measured with a Perkin-Elmer Model 141 polarimeter; the infrared spectrum was recorded on a Nicolet SX-60 FTIR spectrometer; and ultraviolet spectra were obtained with an IBM Model 9420 UV spectrometer. Chromatographic separations were monitored by HPLC using a Waters Assoc. μBondapak C-18 column (0.4 × 30 cm) and 0.05 M pH 6.8 NH_4OAc buffer-MeCN (65:35) as the mobile phase. At a flow rate of 1.5 mL/min, the retention times of oxotomaymycin, PD 125375, and tomaymycin are about 3.3, 3.6, and 5.5 min, respectively.

Isolation of PD 125375 (2). Fermentation broth (24 L) was extracted with 1-butanol and the organic layer was concentrated in vacuo to afford 16 g of a residue. This product was chromatographed over alumina (300 g) using absolute ethanol, EtOH–H_2O (95:5), and MeOH–H_2O (80:20). The latter two eluents afforded, respectively, tomaymycin (127 mg) and oxotomaymycin (222 mg) as crystalline solids.[9] The residue (2.0 g) obtained from the initial absolute ethanol fractions was dissolved in 4 mL of MeOH–H_2O (1:1) and chromatographed over 160 g of C-18 silica gel using MeCN–H_2O (15:85) as the mobile phase. Several 200-mL fractions were collected and each was analyzed by HPLC. PD 125375 was present in fractions 8–11 (800 mL) which were combined and concentrated to 500 mL. Two extractions with 500-mL portions of ethyl acetate afforded 0.52 g of a partially crystalline residue. Recrystallization of this material from ethyl acetate yielded 232 mg of PD 125375 as colorless needles: mp 181–183 °C; MS, m/e 218 (M^+); UV λ^{MeOH}_{max} nm (ϵ) 231 (9505), 273 (12 100); IR ν_{max} (CCl_4) cm^{-1} 3200, 1630, 1560, 1475, 1440; $[\alpha]_D$ +89.8° (c 0.52, MeOH); NMR data are listed in Table I. Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.83. Found: C, 65.82; H, 6.33; N, 12.53.

Single-Crystal X-ray Diffraction Analysis of PD 125375. Preliminary X-ray photographs of **2** displayed orthorhombic diffraction symmetry, and accurate lattice constants of a = 12.479 (4), b = 12.421 (2), and c = 7.057 (1) Å were determined from a least-squares fit of 15 diffractometer measured 2θ values. Systematic extinctions, optical activity, and an approximate density of 1.33 g/cm^3 were uniquely accommodated by space group $P2_12_12_1$ with 1 molecule of formula $C_{12}H_{14}N_2O_2$ forming the asymmetric unit. All unique diffraction maxima with $2\theta < 114°$ were measured by using graphite-monochromated Cu Kα radiation (1.54178 Å) and variable speed, 1° ω-scans. Of the 885 reflections measured in this way, 732 (83%) were judged observed ($F_o > 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects.[10] The structure was solved routinely by using direct methods and all non-hydrogen atoms were clearly visible in the initial E-synthesis. Hydrogen atoms were located in a ΔF-synthesis following partial refinement. Block-diagonal least-squares refinements have converged to a conventional crystallographic residual of 0.086 for the observed data. Additional crystallographic details are available and are described in the paragraph entitled Supplementary Material Available at the end of this paper.

Acknowledgment. The portion of this work performed at Warner-Lambert/Parke-Davis was supported in part by the National Cancer Institute Contract NO1-CM-37614. The Cornell authors thank NSF INT14133 and NIH CA24487 for partial support of this work.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles for PD 125375 (5 pages). Ordering information is given on any current masthead page.

(7) Macura, S.; Wuthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1982**, *46*, 269.

(8) Sørensen, O. W.; Dønstrup, S.; Bildsøe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1984**, *55*, 347.

(9) We thank Dr. Kohsaka for supplying us with samples of tomaymycin and oxotomaymycin for these comparisons which were based on ^{1}H NMR, IR, UV, HPLC, and TLC data.

(10) All crystallographic calculations were done on a PRIME 9950 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 80 and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1980; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a locally modified crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu and G. Van Duyne, Cornell University, 1985.

New Organocuprate-Induced Reduction of the Enol Phosphate Moiety in 1-[(Diethoxyphosphinyl)oxy]-*F*-1-alkene-1-phosphonates: An Efficient Synthesis of (*Z*)-1-Hydryl-*F*-1-alkene-1-phosphonates

Takashi Ishihara,* Takashige Maekawa, Yasuhiro Yamasaki, and Teiichi Ando

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

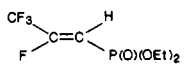
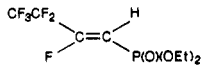
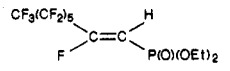
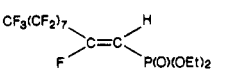
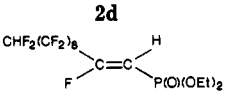
Received July 25, 1986

The replacement of an enol ester function, such as enol acetates, triflates, and phosphates, with a hydrogen or an alkyl group is an important reaction in organic synthesis. In the literature, there exist several methods for such a transformation, which involve a transition-metal-catalyzed cross-coupling reaction,[1] organocopper-mediated reaction,[2]

(1) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246. Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 2531. Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. Sato, M.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1609. Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Tetrahedron Lett.* **1981**, *22*, 4449. Okuda, Y.; Sato, M.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2015. Sahlberg, C.; Quader, A.; Claesson, A. *Tetrahedron Lett.* **1983**, *24*, 5137. Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271. Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 4821. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yashida, Z. *Tetrahedron Lett.* **1986**, *27*, 955. Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277.

0022-3263/87/1952-0300$01.50/0

Table I. Synthesis of (*Z*)-1-Hydryl-*F*-1-alkene-1-phosphonates 2

alkenephosphonate 2	yield, %	J_{H-F},[a] Hz	^{31}P NMR,[b] δ
 2a	65	40.0	7.54
 2b	81	38.9	7.07
 2c	62	37.9	7.11
 2d	80	39.3	7.08
 2e	70	40.5	6.97

[a] Determined by ^1H and/or ^{19}F NMR analysis. [b] Expressed in ppm downfield from external H_3PO_4.

and alkali metal–ammonia or amine reduction reaction.[3]

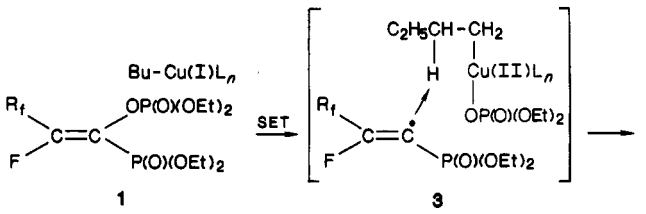
In our continuing effort to develop new methods for the synthesis of fluorine-containing functionalized olefinic compounds as well as to extend their synthetic utility,[4] we have found that diethyl (*Z*)-1-[(diethoxyphosphinyl)-oxy]-*F*-1-alkene-1-phosphonates 1, accessible from *F*-alkanoic acid chlorides,[5] readily react with an organocuprate reagent to afford the corresponding (*Z*)-1-hydryl-*F*-1-alkene-1-phosphonates 2 in good yields.

This paper describes a novel, efficient reduction of the enol phosphate moiety in 1 with lithium dibutylcuprate, which provides a convenient access for the synthesis of fluorinated alkenephosphonates from *F*-alkanoic acid chlorides.

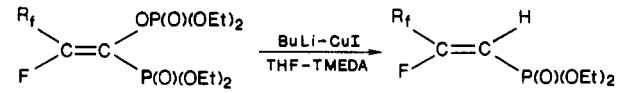
Results and Discussion

The starting phosphonates 1 were prepared in high yields by the reaction of *F*-alkanoic acid chlorides with 2 equiv of triethyl phosphite.[5] When the phosphonate 1 was treated with an excess of lithium dibutylcuprate[6] in tetrahydrofuran (THF) at −78 °C, the corresponding (*Z*)-1-hydryl-*F*-1-alkene-1-phosphonate 2 was obtained in good yield.[7] The stereochemistry of 2 could be determined on the basis of the magnitudes of coupling constants between the vinylic fluorine and hydrogen atoms in ^1H and ^{19}F NMR spectra. Table I summarizes the results of the reaction, together with the coupling constants and phosphorus chemical shifts of the products.

Scheme I



2 + Cu(I)OP(O)(OEt)$_2$L$_n$ + $C_2H_5CH{=}CH_2$



1a: $R_f = CF_3$
b: $R_f = CF_3CF_2$
c: $R_f = CF_3(CF_2)_5$
d: $R_f = CF_3(CF_2)_7$
e: $R_f = CHF_2(CF_2)_8$

2

The ratio of 1.7–1.8 of butyllithium to cuprous iodide was essential to the present reaction, because the use of the stoichiometric ratio (2.0) of the reagents resulted in a substantial decrease of the yields of 2 and in contamination by unidentified byproducts. In addition, the fact that both the starting phosphonates 1 and the products 2 reacted with butyllithium or butylmagnesium bromide to give complex products made us avoid the stoichiometric cuprate reagent. Other organocuprate reagents such as lithium dimethyl- and diphenylcuprate[6] were not effective for the reaction.[8] Either THF or diethyl ether could be used as solvent. The addition of tetramethylethylenediamine (TMEDA) to the solvent improved the reproducibility of the reaction. The reaction occurred selectively on the enol phosphate moiety in 1 and with complete retention of configuration. It is noteworthy that no butylated product was obtained in any case, because the similar reaction of fluorine-free enol phosphates with lithium dialkylcuprate gives the corresponding alkylated alkenes.[2a-d]

When the reaction was quenched with deuterium oxide or allyl bromide, neither deuteriated nor allylated phosphonates were formed at all in the reaction mixture but the phosphonates 2 were obtained in good yields. These results strongly suggest that this type of reduction does not proceed through a carbanionic intermediate that may be formed by an enol phosphate–copper exchange.[9] Moreover, even when the reaction was conducted in THF-d_8 under the same reaction conditions, the deuterium-incorporated products were not produced. These findings allow us to derive a plausible mechanism for the present reaction such as depicted in Scheme I. Thus, a single electron transfer (SET) from dibutylcuprate reag-

(2) (a) Blaszczak, L.; Winkler, J.; O'Kuhn, S. *Tetrahedron Lett.* **1976**, 4405. (b) Sum, F. W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431. (c) Sum, F. W.; Weiler, L. *Tetrahedron, Suppl.* **1981**, *37*, 303. (d) Belmont, D. T.; Paquette, L. A. *J. Org. Chem.* **1985**, *50*, 4102. (e) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1980**, *21*, 4313. (f) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979. (g) Claesson, A.; Quader, A.; Sahlberg, C. *Tetrahedron Lett.* **1983**, *24*, 1297. (h) Fugami, K.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 2161.

(3) Fetizon, M.; Jurion, M.; Anh, N. T. *J. Chem. Soc., Chem. Commun.* **1969**, 112.

(4) (a) Yamana, M.; Ishihara, T.; Ando, T. *Tetrahedron Lett.* **1983**, *24*, 507. (b) Ishihara, T.; Maekawa, T.; Ando, T. *Tetrahedron Lett.* **1983**, *24*, 4229. (c) Ishihara, T.; Yamana, M.; Ando, T. *Tetrahedron Lett.* **1983**, *24*, 5657. (d) Ishihara, T.; Maekawa, T.; Ando, T. *Tetrahedron Lett.* **1984**, *25*, 1377. (e) Ishihara, T.; Yamasaki, Y.; Ando, T. *Tetrahedron Lett.* **1985**, *26*, 79. (f) Yamasaki, Y.; Maekawa, T.; Ishihara, T.; Ando, T. *Chem. Lett.* **1985**, 1387. (g) Ishihara, T.; Maekawa, T.; Ando, T. *Tetrahedron Lett.* **1986**, *27*, 357. (h) Ishihara, T.; Yamasaki, Y.; Ando, T. *Tetrahedron Lett.* **1986**, *27*, 2879.

(5) Ishihara, T.; Maekawa, T.; Yamasaki, Y.; Ando, T. *J. Fluorine Chem.*, in press.

(6) The term is employed for convenience, though the organocopper reagents used in this study do not precisely correspond to a stoichiometric cuprate reagent.

(7) On treatment with lithium dibutylcuprate under similar conditions, the phosphonate 2 was left unchanged and was recovered almost quantitatively.

(8) The reagents prepared from butylmagnesium bromide or methylmagnesium iodide and cuprous iodide also did not effect the present reaction, many complex products being formed.

(9) The related halogen–copper exchange reactions have been reported. For example, see: House, H. O.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 5495. Kitatani, K.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1976**, *98*, 2362. Yamamoto, H.; Kitatani, K.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 5816. Scott, F.; Mafunda, B. G.; Normant, J. F.; Alexakis, A. *Tetrahedron Lett.* **1983**, *24*, 5767.

ent[10] to 1 and successive cleavage of a vinyl carbon–oxygen bond could occur to generate an alkenyl radical intermediate 3. This transient intermediate might then abstract a hydrogen atom from the butyl group of the resulting organocopper species, giving the product 2 along with 1-butene.[11]

In summary, diethyl (*Z*)-1-[(diethoxyphosphinyl)oxy]-*F*-1-alkene-1-phosphonates 1, easily prepared from *F*-alkanoic acid chlorides and diethyl phosphite, undergo reduction efficiently with lithium dibutylcuprate[6] to give good yields of the corresponding (*Z*)-1-hydryl-*F*-1-alkene-1-phosphonates 2, which have been shown to be good precursors for synthesizing a variety of organofluorine compounds.[4d-g]

Experimental Section

Infrared spectra (IR) were taken on a Shimadzu IR-400 infrared spectrometer using a polystyrene film for calibration. ^{1}H NMR spectra were recorded with a Varian EM-390 or a JEOL PMX-60si spectrometer for solutions in carbon tetrachloride (CCl_4) with tetramethylsilane (Me_4Si) as an internal standard. A Varian EM-390 spectrometer or a JEOL FX-90Q computer-controlled spectrometer was used to measure ^{19}F NMR spectra in CCl_4 or chloroform-*d* ($CDCl_3$) with internal trichlorofluoromethane ($CFCl_3$). ^{31}P NMR spectra were obtained on a JEOL FX-90Q computer-controlled spectrometer in $CDCl_3$ with 85% phosphoric acid as an external reference. Mass spectra were determined with a Hitachi RMS-4 mass spectrometer operating at an ionization potential of 70 eV.

Materials. All chemicals were of reagent grade and used without further purification. Solvents were distilled (or vacuum-distilled) through a 25-cm Vigreux column and, if necessary, were purified in the conventional manner prior to use. *F*-Alkanoic acid chlorides were prepared by the literature method.[12] The starting fluoroalkenephosphonates 1 were obtained in 65–80% yields according to our recently reported method.[5]

General Procedure for the Reaction of (*Z*)-1-[(Diethoxyphosphinyl)oxy]-*F*-1-alkene-1-phosphonate 1 with Lithium Dibutylcuprate[6] Reagent. In a four-necked flask fitted with a thermometer, a mechanical stirrer, an inlet tube for nitrogen, and a rubber septum were placed cuprous iodide (23.8 g, 125.0 mmol), anhydrous TMEDA (14.5 g, 125.0 mmol), and 250 mL of dry THF. This suspension was cooled to −78 °C by immersing in a dry ice–methanol bath, and butyllithium (147 mL, 220.0 mmol) in hexane (1.5 M) was gradually added to it by use of a syringe. After the reaction mixture was stirred for 30 min at −78 °C, a solution of 1 (50.0 mmol) in 25 mL of dry THF was added to the resulting dark-brown solution at such a rate that the reaction temperature did not rise above −60 °C. The whole mixture was stirred for 15 min at −78 °C. To this reaction mixture, which had been brought to −50 to −40 °C, was added successively 10 mL of water and 200 mL of a saturated aqueous solution of ammonium chloride. After being stirred for a while at room temperature, the mixture was subjected to extraction with ether (4 × 100 mL). The ethereal extracts were washed three times with water, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residual oil was distilled in vacuo or chromatographed on silica gel (Wako gel C-200) by using ether as an eluent to give analytically pure product 2.

Diethyl (*Z*)-1-hydryl-*F*-1-propene-1-phosphonate (2a): 65% yield; bp 60 °C (17 mmHg); IR (film) 2950 (m), 1700 (m), 1485 (w), 1450 (m), 1400 (m), 1365 (s), 1250 (s), 1215 (s), 1165 (s), 1105 (m), 1060 (s), 1030 (vs), 975 (s), 830 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.2 Hz, 6 H), 4.10 (dq, J = 7.2 and 7.2 Hz, 4 H), 5.83 (dd, J = 40.0 and 2.9 Hz, 1 H); ^{19}F NMR (CCl_4) δ −73.9 (d, J = 9.9 Hz, 3 F), −108.8 (ddq, J = 40.0, 9.9 and 2.8 Hz, 1 F); ^{31}P NMR ($CDCl_3$) δ 7.54; mass spectrum, m/e (relative intensity) 249 ($M^+ - 1$, 1.9), 195 (100). Anal. Calcd for $C_7H_{11}F_4O_3P$: C, 33.61; H, 4.43; F, 30.38. Found: C, 33.83; H, 4.59; F, 30.04.

Diethyl (*Z*)-1-hydryl-*F*-1-butene-1-phosphonate (2b): 81% yield; bp 65 °C (17 mmHg); IR (film) 2980 (m), 2930 (m), 1685 (s), 1475 (w), 1440 (m), 1390 (m), 1365 (m), 1340 (s), 1325 (s), 1260 (s), 1205 (vs), 1165 (s), 1090 (s), 1040 (vs), 970 (s), 825 (m), 715 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.4 Hz, 6 H), 4.10 (dq, J = 7.4 and 7.4 Hz, 4 H), 5.89 (dd, J = 38.9 and 2.7 Hz, 1 H); ^{19}F NMR (CCl_4) δ −84.3 (dt, J = 7.0 and 2.1 Hz, 3 F), −104.9 (ddtq, J = 38.9, 7.0, 12.4, and 2.8 Hz, 1 F), −121.8 (dm, J = 12.4 Hz, 2 F); ^{31}P NMR ($CDCl_3$) δ 7.07; mass spectrum, m/e (relative intensity) 299 ($M^+ - 1$, 1.6), 245 (100). Anal. Calcd for $C_8H_{11}F_6O_3P$: C, 32.01; H, 3.69; F, 37.98. Found: C, 32.22; H, 3.86; F, 37.77.

Diethyl (*Z*)-1-hydryl-*F*-1-octene-1-phosphonate (2c): 62% yield; IR (film) 3000 (m), 2950 (m), 1690 (m), 1485 (w), 1450 (m), 1400 (m), 1375 (m), 1345 (m), 1250 (vs), 1205 (vs), 1150 (s), 1100 (s), 1030 (s), 980 (s), 835 (m), 815 (m), 740 (m), 720 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.38 (t, J = 7.5 Hz, 6 H), 4.13 (dq, J = 7.5 and 7.5 Hz, 4 H), 5.91 (dd, J = 37.9 and 3.0 Hz, 1 H); ^{19}F NMR (CCl_4) δ −81.6 (br s, 3 F), −103.5 (dm, J = 37.9 Hz, 1 F), −118.3 (dt, J = 12.7 and 12.7 Hz, 2 F), −121.2 to −124.2 (m, 6 F), −125.0 (m, 2 F); ^{31}P NMR ($CDCl_3$) δ 7.11. Anal. Calcd for $C_{12}H_{11}F_{14}O_3P$: C, 28.82; H, 2.22; F, 53.18. Found: C, 28.63; H, 2.36; F, 52.92.

Diethyl (*Z*)-1-hydryl-*F*-1-decene-1-phosphonate (2d): 80% yield; IR (film) 3000 (m), 2950 (m), 1695 (m), 1485 (w), 1450 (w), 1400 (m), 1380 (m), 1350 (m), 1240 (s), 1205 (vs), 1155 (s), 1120 (s), 1045 (s), 1030 (s), 980 (s), 830 (m), 810 (m), 715 (m), 705 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.2 Hz, 6 H), 4.13 (dq, J = 7.2 and 7.2 Hz, 4 H), 5.92 (dd, J = 39.3 and 2.8 Hz, 1 H); ^{19}F NMR (CCl_4) δ −81.8 (t, J = 9.0 Hz, 3 F), −103.6 (dm, J = 39.3 Hz, 1 F), −118.3 (br s, 2 F), −121.0 to −124.3 (m, 10 F), −126.7 (br s, 2 F); ^{31}P NMR ($CDCl_3$) δ 7.08. Anal. Calcd for $C_{14}H_{11}F_{18}O_3P$: C, 28.02; H, 1.85; F, 56.98. Found: C, 27.91; H, 1.95; F, 56.79.

Diethyl (*Z*)-1,11-dihydryl-*F*-1-undecene-1-phosphonate (2e): 70% yield; IR (film) 2990 (m), 2945 (m), 1686 (m), 1482 (w), 1445 (w), 1394 (m), 1340 (m), 1250 (s), 1207 (vs), 1150 (vs), 1050 (s), 1020 (s), 970 (m), 827 (m), 800 (m), 729 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.5 Hz, 6 H), 4.13 (dq, J = 7.5 and 7.5 Hz, 4 H), 5.87 (dd, J = 40.5 and 3.0 Hz, 1 H), 6.05 (tt, J = 54.5 and 5.3 Hz, 1 H); ^{19}F NMR ($CDCl_3$) δ −102.3 (br d, J = 40.5 Hz, 1 F), −118.3 (br s, 2 F), −122.1 to −122.9 (br m, 10 F), −123.7 (br s, 2 F), −129.7 (br s, 2 F), −137.5 (br d, J = 54.5 Hz, 2 F); ^{31}P NMR ($CDCl_3$) δ 6.97. Anal. Calcd for $C_{15}H_{12}F_{19}O_3P$: C, 28.50; H, 1.91; F, 57.10. Found: C, 28.71; H, 2.13; F, 56.78.

(10) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. Ashby, E. C.; DePriest, R. N.; Tuncay, A.; Srivastava, S. *Tetrahedron Lett.* **1982**, *23*, 5251.
(11) The formation of 1-butene has not been confirmed successfully.
(12) Tiers, G. V. D. *J. Org. Chem.* **1964**, *29*, 2038.

The Bridgehead Decalin Radicals: An MM2 and MNDO Study

Henry A. Kurtz,* Roger V. Lloyd,* and Richard Vaughan Williams*

Department of Chemistry, Memphis State University, Memphis, Tennessee 38152

Received July 28, 1986

Introduction

ESR evidence has recently been presented[1] which indicates the existance of distinguishable bridgehead radicals derived from *cis*- and *trans*-decalin. They are thought to be nonplanar at the radical sites, but considerably flattened from normal tetrahedral geometry. Chemical evidence of this was presented earlier by Bartlett et al.[2] and by Greene and Lowry.[3] Greene[3] studied the free radical decomposition of the *cis*- and *trans*-9-decalylcarbinyl hypochlorites to give the 9-chlorodecalins and deduced that two different 9-decalyl radical intermediates were required. They concluded that radicals which were either pyramidal or planar at the radical sites could account for the observed results.

(1) Lloyd, R. V.; Williams, R. V. *J. Phys. Chem.* **1985**, *89*, 5379.
(2) Bartlett, P. D.; Pincock, R. E.; Rolston, J. H.; Schindel, W. G.; Singer, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 2590.
(3) Greene, F. D.; Lowry, N. N. *J. Org. Chem.* **1967**, *32*, 875.

0022-3263/87/1952-0302$01.50/0