JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2007,** *55,* 6933−6939 **6933**

Synthesis of [3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2*H*-2λ^5-benzo[*e*][1,3,2]oxazaphosphinin-2-yl]-(aryl/alkyl) Methanols and Their Bioactivity on Sugarcane Smut

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Synthesis of some new substituted [3-(3-chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2*H*-2λ^5-benzo[*e*]-[1,3,2]oxazaphosphinin-2-yl]-(aryl/alkyl)methanols (**7a**−**k**) based on the Pudovick reaction was accomplished in the presence of niobium pentoxide (Nb_2O_5) without using an external chiral ligand. Nb_2O_5 appears to form the metal complex intermediate catalyst system (**6**) by reacting with 3-(3-chloro-4-fluoro-phenyl)-3,4-dihydrobenzo[*e*][1,3,2]oxazaphosphinine-2-oxide (**4**), which not only directs the Pudovick addition reactions of aldehyde but also increases the yields and purity of the products. These compounds exhibited a lethal effect on whip smut of sugarcane and were degraded in the environment in the presence of bacteria and fungi to nontoxic phosphate residues that act as possible plant nutrients. Thus, a new class of benzooxazaphosphininyl methanol derivatives that act in synergy both as antipathogens and as plant nutrients in the environment have been discovered.

KEYWORDS: Pudovick reaction; benzooxazaphosphinyl methanols; niobium pentoxide; whip smut.

INTRODUCTION

Sugarcane is the most important commercial crop of India, covering an area of about 3.6 million hectares with an annual cane yield of about 237.1 million tonnes. The annual production of raw sugar is about 10−11 million tons (*1*). The sugarcane industry is in critical transition from an aggressive biosecurity strategy to that of its economic industrial management (*2*). Over 100 fungi, 10 bacteria, 10 virus, and about 50 nematode species are important sugarcane pests in different parts of the world. Today, sugarcane agriculture all over the world is severely damaged by whip smut (*3*). Sugarcane smut caused by the fungus *Ustilago scitaminea* was first noted in South Africa in 1877. It is highly infectious and systemic and can spread even by wind. It is a serious sugarcane disease which can reduce yields by 30−100% (*1*−*3*). No chemical currently used as a pesticide has been found to be effective against this disease once it has infected the plants in the fields. Moreover, the applied chemical pesticides are long-lived and cause toxic effects through the food cycle in various life forms. In this context, our continuous quest for the development of ecofriendly antimicrobial and xenobiotics resulted in the synthesis of some effective, short-lived, and biodegradable pesticides (*4*), 2-substituted [3-(3-chloro-4-fluoro-phenyl)-2-oxo-3,4-dihydro-2*H*-2λ^5-benzo[*e*][1,3,2]oxazaphosphinin-2yl]-(aryl/alkyl)methanols (**7a**−**k**) and their epoxides (**8a**/**b**). Our endevour for the preparation of the title compounds **7a**−**k** and **8a**/**b** was accomplished by the Pudovik addition (*5*) of dialkyl/aryl phosphates (**4**) with the carbonyl compounds (**5**) in the presence of a triethylamine base and a Nb_2O_5 catalyst. The rationale for their synthesis is that the oxazaphosphonate pharmacophore present was expected to impart significant biological activity since several organophosphorus compounds containing this structural unit (**Figure 1**) have proven activity against bacteria, viruses, fungi, cancer, and many other disease manifestations (*6*−*8*). The presence of a 3-chloro-4-fluorophenyl group at the nitrogen and α-hydroxyaryl/oxiranyl moiety at the phosphorus of the phosphoryl pharmacophore structural unit (Figure 1) embedded in the oxazaphosphinin ring system of the title compounds (**7a**−**k**) may significantly reinforce bioactivity (*9*). In addition, the α-hydroxy carbon provides the site for further elaboration of these molecules that are useful as reagents in organic synthesis and industry. The configuration at the α carbon, being important for biological activity (*10*) and synthesis of chiral, nonracemic α-hydroxy phosphoryl compounds, has also gained serious attention.

MATERIALS AND METHODS

Experimental Chemistry. Solvents used were purified by the established procedures (*11*). Progress of the reaction and purity of the compounds were monitored by thin-layer chromatography (TLC) using hexane-ethyl acetate (3:2) as an irrigating system and iodine as a visualizing agent. Melting points were determined in open capillary

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10.1021/jf070850z CCC: $37.00
Published on Web 07/28/2007

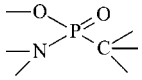

Figure 1. Oxazaphosphoryl pharmacophore.

tubes on a Mel-temp apparatus and were uncorrected. Microanalyses were performed on a Yanaca CHN Corder MT-3 elemental analyzer. Infrared spectra (γ_{max} in cm^{-1}) were recorded as KBr pellets on a JASCO FT/IR-5300. ^1H and ^{13}C NMR spectra were recorded on a GEMINI 300 (300 and 75.46 MHz), and ^{31}P NMR spectra were recorded on a DRX 300 (121.5 MHz) using acetone (d_6) and DMSO-(d_6) (DMSO = dimethylsulfoxide). The ^1H and ^{13}C chemical shifts were referenced to tetramethylsilane and 85% H_3PO_4 for ^{31}P chemical shifts. Mass spectra were recorded on a Jeol SX 102 DA/600 mass spectrometer using argon/xenon (6 kV, 10 mA) as the fast atom bombardment (FAB) gas.

Synthesis. *3-(3-Chloro-4-fluorophenyl)-3,4-dihydrobenzo[e]-[1,3,2]oxazaphosphinine-2-oxide (**4**).* A solution of PBr_3 (0.93 mL, 2.7 g, 0.01 mol) in dry toluene (10 mL) was added dropwise over a period of 15 min to a stirred solution of α-(3-chloro-4-fluoroaniline)-2-cresol (**1**) (2.51 g, 0.01 mol) (*8*) and triethylamine (2.78 mL, 2.02 g, 0.02 mol) in dry toluene (30 mL) at 0 °C. After addition, stirring was continued for 3 h at 50 °C. Triethylamine hydrobromide was filtered off. To the filtrate containing 2-bromo-3-(3-chloro-4-fluorophenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3,2]oxazaphosphinine (**2**) was added triethylamine (1.34 mL, 1.01 g, 0.01 mol), and the solution was stirred at 0 °C. Water (0.018 g, 0.01 mol) was added through a septum, using a Hamilton 50 μL syringe, to the vessel cooled in an ice-salt bath at 0 °C with stirring for an additional 2 h at 25 °C to obtain **3** and **4**. The solution was dried over anhydrous Na_2SO_4 for 2 h, decanted, and used for further reaction (**Scheme 1**).

Synthesis of 7a−k. *[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e][1,3,2]oxazaphosphinin-2-yl]phenylmethanol (**7a**).* The mixture of **3** and **4** (0.01 mol), alkyl/aryl aldehyde (**5**) (0.01 mol), Et_3N (0.05 mol), and a catalytic quantity of Nb_2O_5 in toluene (20 mL) was stirred for 4 h at 50 °C. (**Table 1**). After completion of the reaction as indicated by TLC, the reaction mixture was filtered, and the filtrate was adsorbed on silica gel G (60−120 mesh). Compound **7a** was obtained in the pure state by column chromatography using a 2-ft-length and 0.5-ft-diameter glass column and 3:1 ethyl acetate/hexane as the eluent (**Scheme 1**).

mp: 116−118 °C. IR (KBr): 3260 (−$OH_{aliphatic}$), 1218 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (DMSO-d_6): δ 7.18−6.50 (m, 12H, Ar−H), 5.11−5.07 (m, 2H, −CH_2−), 4.55 (s, 1H, *H*−C−OH), 3.57 (brs, 1H, H−C−O*H*). ^{13}C NMR (DMSO-d_6): δ 41.48 (C-4), 128.35 (C-5), 122.32 (C-6), 127.74 (C-7), 116.68 (C-8), 155.10 (C-9), 125.01(C-10), 146.42 (C-1′), 116.96 (C-2′), 121.82 (C-3′), 150.47 (C-4′), 118.84 (C-5′), 114.97 (C-6′), 137.23 (C-1″), 129.63 (C-2″ & C-6″), 129.01 (C-3″ & C-5″), 132.20 (C-4″), 70.80 (H-*C*-OH). ^{31}P NMR (DMSO-d_6): δ −11.02. FAB MS: *m*/*z* (%) 405 (5) [$M^{+\bullet}$+2], 403 (13) [$M^{+\bullet}$], 401 (3), 327 (5), 281 (11), 251 (9), 246 (7), 147 (38), 123 (16), 107 (19), 73 (100). Anal. Calcd for $C_{20}H_{16}FClNO_3P$: C, 59.49; H, 3.99. Found: C, 59.56; H, 4.01.

Compounds **7b−k** were prepared by the above procedure using respective aldehydes.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-4-chlorophenylmethanol (**7b**).* mp: 230(d)°C. IR (KBr): 3362 (−$OH_{aliphatic}$), 1222 (P═O), 765 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.12−6.73 (m, 11H, Ar−H), 5.10−4.92 (m, 2H, −CH_2−), 3.93 (s, 1H, *H*−C−OH), 3.53 (brs, 1H, H−C−O*H*). ^{13}C NMR (acetone-d_6): δ 42.71(C-4), 127.89 (C-5), 122.42 (C-6), 126.68 (C-7), 118.94 (C-8), 156.78 (C-9), 125.11(C-10), 144.57 (C-1′), 118.87 (C-2′), 122.18 (C-3′), 153.77 (C-4′), 118.07 (C-5′), 112.91 (C-6′), 135.25(C-1″), 131.20 (C-2″ and C-6″), 129.79 (C-3″ and C-5″), 142.89 (C-4″), 61.83 (H−*C*−OH). ^{31}P NMR (acetone-d_6): δ −10.85. FAB MS: *m*/*z* (%) 441 (3) [$M^{+\bullet}$+4], 439 (12) [$M^{+\bullet}$+2], 437 (18) [$M^{+\bullet}$], 326 (18), 280 (44), 251 (37), 145 (100), 107 (21). Anal. Calcd for $C_{20}H_{15}FCl_2NO_3P$: C, 54.78; H, 3.44. Found: C, 54.72; H, 3.47.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-4-bromophenylmethanol (**7c**).* mp: 178−180 °C. IR (KBr): 3385 (−$OH_{aliphatic}$), 1224 (P═O), 768 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.22−6.53 (m, 11H, Ar−H), 5.18−5.08 (m, 2H, −CH_2−), 4.55 (s, 1H, *H*−C−OH), 3.85 (brs, 1H, H−C−O*H*). ^{13}C NMR (acetone-d_6): δ 43.68 (C-4), 130.18 (C-5), 123.48 (C-6), 126.67 (C-7), 119.02 (C-8), 155.57 (C-9), 125.16 (C-10), 142.54 (C-1′), 118.37 (C-2′), 123.15 (C-3′), 155.34 (C-4′), 118.39 (C-5′), 114.78 (C-6′), 136.25(C-1″), 131.20 (C-2″ and C-6″), 135.79 (C-3″ and C-5″), 125.18 (C-4″), 63.13 (H−*C*−OH). ^{31}P NMR (acetone-d_6): δ −4.20. Anal. Calcd for $C_{20}H_{15}BrFClNO_3P$: C, 49.74; H, 3.13. Found: C, 49.76; H, 3.19.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-4-hydroxyphenylmethanol (**7d**).* mp: 97−99 °C. IR (KBr): 3254 (−$OH_{aliphatic}$), 1223 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.82−6.61 (m, 11H, Ar−H), 5.12−4.98 (m, 2H, −CH_2−), 4.63 (s, 1H, *H*−C−OH), 3.67 (brs, 1H, H−C−O*H*), 9.83 (s, 1H, 4″−O*H*). ^{13}C NMR (acetone-d_6):δ 43.80 (C-4), 129.28 (C-5), 120.34 (C-6), 128.47 (C-7), 115.91 (C-8), 156.24 (C-9), 125.77 (C-10), 143.42 (C-1′), 117.54 (C-2′), 120.32 (C-3′), 152.54(C-4′), 117.26 (C-5′), 114.72 (C-6′), 129.80 (C-1″), 130.23 (C-2″ and C-6″), 115.86 (C-3″ and C-5″), 159.34 (C-4″), 70.25 (H−*C*−OH). ^{31}P NMR (acetone-d_6): δ −7.48. Anal. Calcd for $C_{20}H_{16}FClNO_4P$: C, 57.19; H, 3.83. Found: C, 57.25; H, 3.88.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-2-hydroxyphenylmethanol (**7e**).* mp: 240(d)°C. IR (KBr): 3260 (−$OH_{aliphatic}$), 1221 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.17−6.50 (m, 11H, Ar−H), 5.03−4.85 (m, 2H, −CH_2−), 4.54 (s, 1H, *H*−C−OH), 3.51(brs, 1H, H−C−O*H*), 9.57 (s, 1H, 2″−O*H*).^{13}C NMR (DMSO-d_6): δ 41.67 (C-4), 128.37 (C-5), 118.88 (C-6), 127.77 (C-7), 115.70 (C-8), 157.23 (C-9), 124.66 (C-10), 144.57 (C-1′), 116.98 (C-2′), 118.88 (C-3′), 154.77 (C-4′), 116.70 (C-5′), 114.91 (C-6′), 124.22 (C-1″), 153.12 (C-2″), 119.74 (C-3″), 136.41 (C-4″), 121.39 (C-5″), 128.37 (C-6″), 71.92 (H−*C*−OH). ^{31}P NMR (acetone-d_6): δ −7.57. Anal. Calcd for $C_{20}H_{16}FClNO_4P$: C, 57.19; H, 3.83. Found: C, 57.23; H, 3.79.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-2-hydroxy-4-chlorophenylmethanol (**7f**).* mp: 78−80 °C. IR (KBr): 3258 (−$OH_{aliphatic}$), 1224 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.27−6.61 (m, 10H, Ar−H), 5.01−4.89 (m, 2H, −CH_2−), 4.63 (s, 1H, *H*-C−OH), 3.08 (brs, 1H, H−C−O*H*), 8.66 (s, 1H, 2″−O*H*). ^{13}C NMR (acetone-d_6): δ 43.15 (C-4), 128.30 (C-5), 119.75 (C-6), 126.58 (C-7), 116.74 (C-8), 156.94 (C-9), 124.37 (C-10), 140.57 (C-1′), 117.98 (C-2′), 111.76 (C-3′), 154.21 (C-4′), 117.27 (C-5′), 113.82 (C-6′), 122.49 (C-1″), 158.52 (C-2″), 116.76 (C-3″), 142.80 (C-4″), 120.85 (C-5″), 133.28 (C-6″), 61.02 (H−*C*−OH). ^{31}P NMR (acetone-d_6): δ −7.92. Anal. Calcd for $C_{20}H_{15}FCl_2NO_4P$: C, 52.85; H, 3.32. Found: C, 52.79; H, 3.39.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-3-hydroxy-4-methoxyphenylmethanol (**7g**).* mp:130−131 °C. IR (KBr): 3256 (−$OH_{aliphatic}$), 1222 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.46−6.57 (m, 10H, Ar−H), 5.13−5.04 (m, 2H, −CH_2−), 4.80 (s, 1H, *H*-C−OH), 3.80 (brs, 1H, H−C−O*H*), 9.81 (s, 1H, 3″−O*H*), 3.91 (s, 3H, −OCH_3). ^{13}C NMR (acetone-d_6): δ 43.69 (C-4), 128.84 (C-5), 120.28 (C-6), 127.02 (C-7), 115.75 (C-8), 156.00 (C-9), 124.77 (C-10), 143.57 (C-1′), 117.56 (C-2′), 119.26 (C-3′), 154.27 (C-4′), 117.27 (C-5′), 114.12 (C-6′), 129.43 (C-1″), 120.29 (C-2″), 142.79 (C-3″), 156.80 (C-4″), 115.75 (C-5″), 134.28 (C-6″), 67.47 (H−*C*−OH), 55.03 (−O*C*H_3). ^{31}P NMR (acetone-d_6): δ −8.83. FAB MS: *m*/*z* (%) 451 (4) [$M^{+\bullet}$+2], 449 (13) [$M^{+\bullet}$], 327 (38), 281 (29), 251 (26), 228 (47), 147 (100), 73 (38). Anal. Calcd for $C_{21}H_{18}FClNO_5P$: C, 56.05; H, 4.03. Found: C, 56.08; H, 4.02.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-3-nitrophenylmethanol (**7h**).* mp:150−152 °C. IR (KBr): 3269 (−$OH_{aliphatic}$), 1222 (P═O), 729 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 8.72−7.91 (m, 11H, Ar−H), 5.16−4.92 (m, 2H, −CH_2−), 4.63 (s, 1H, *H*−C−OH), 2.94 (brs, 1H, H−C−O*H*). ^{13}C NMR (acetone-d_6): δ 43.77(C-4), 129.16 (C-5), 120.32 (C-6), 128.89 (C-7), 115.91 (C-8), 157.23 (C-9), 124.61 (C-10), 142.82 (C-1′), 117.56 (C-2′), 120.34 (C-3′), 154.93 (C-4′), 117.34 (C-5′), 114.15 (C-6′), 138.64 (C-1″), 124.61 (C-2″), 150.12 (C-3″), 129.16 (C-4″), 127.55 (C-5″), 135.29 (C-6″), 87.90 (H-*C*-OH). ^{31}P NMR (acetone-d_6): δ −9.22. FAB MS: *m*/*z* (%) 450 (5) [$M^{+\bullet}$+2], 448 (16)

Scheme 1 . Synthetic Scheme for Benzoxazaphosphinin-2-yl-(aryl/alkyl) Methanols **7a**–**k**

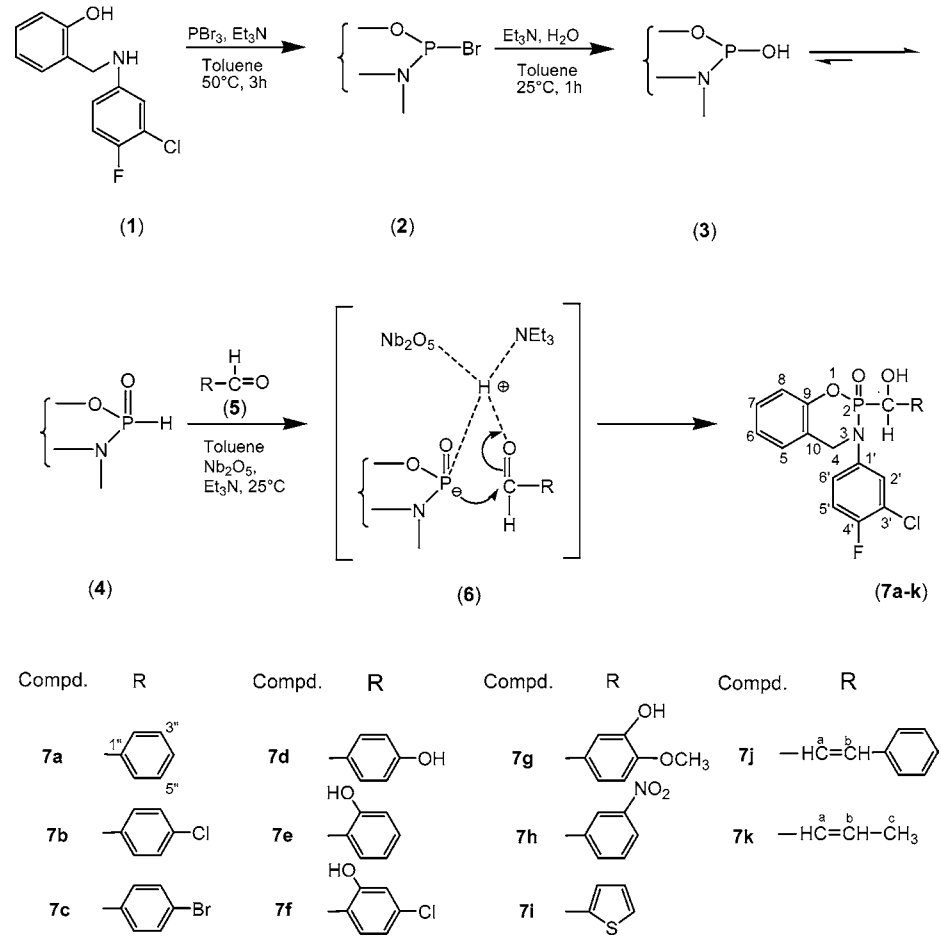

Table 1. Effect of Nb_2O_5 on the Reaction Time and Yield of Compounds **7a**–**k**

S.No of compd.		7a	7b	7c	7d	7e	7f	7g	7h	7i	7j	7k
with out Nb_2O_5	time period in hours	2.5	3.5	3	2	2	2.30	2	3.15	2	17	20
	yields %	65	55	53	56	51	57	59	61	57	42	27
with Nb_2O_5	time period in hours	2	2.15	2	1.30	1.75	2	1.15	2.5	1	10.30	15
	yields %	92	73	75	93	85	76	83	81	71	97	88

[$M^{+\bullet}$], 326 (33), 293 (3), 280 (46), 251 (59), 233 (24), 145 (100). Anal. Calcd for $C_{20}H_{15}FClN_2O_5P$: C, 53.52; H, 3.36. Found: C, 53.57; H, 3.37.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ⁵-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]thiophenemethanol (**7i**).* mp: 118−119 °C. IR (KBr): 3258 (−$OH_{aliphatic}$), 1201 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.25−6.60 (m, 10H, Ar−H), 5.21−5.09 (m, 2H, $-CH_2-$), 4.62 (s, 1H, *H*−C−OH), 3.22 (brs, 1H, H−C−O*H*). ^{13}C NMR ($CDCl_3$): δ 43.68 (C-4), 129.47 (C-5), 120.71 (C-6), 128.83 (C-7), 115.85 (C-8), 155.98 (C-9), 124.56 (C-10), 143.57 (C-1′), 117.56 (C-2′), 120.71 (C-3′), 158.00 (C-4′), 117.27 (C-5′), 114.20 (C-6′), 139.16 (C-1″), 133.36 (C-2″), 130.36 (C-3″), 131.54 (C-4″), 61.84 (H-*C*-OH). ^{31}P NMR (acetone-d_6): δ −9.43. FAB MS: *m*/*z* (%) 411(7) [$M^{+\bullet}$+ 2], 409(18) [$M^{+\bullet}$], 327 (4), 281 (8), 251 (11), 207 (12), 193 (5), 147 (33), 73 (100). Anal. Calcd for $C_{18}H_{14}FClNO_3PS$: C, 52.82; H, 3.44. Found: C, 52.87; H, 3.47.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ⁵-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-3-phenyl-2-propen-1-ol (**7j**).* mp: 101−103 °C. IR (KBr): 3298 (−$OH_{aliphatic}$), 1222 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.12−6.76 (m, 12H, Ar−H), 5.17−5.02 (m, 2H, $-CH_2-$), 4.80 (s, 1H, *H*−C−OH), 3.22 (brs, 1H, H−C−O*H*), 6.69−6.60 (m, 2H, $-^aCH=^bCH-$). ^{13}C NMR: Solubility was too low for recording. ^{31}P NMR (acetone-d_6): δ −8.79. Anal. Calcd for $C_{22}H_{18}FClNO_3P$: C, 61.47; H, 4.22. Found: C, 61.53; H, 4.19.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ⁵-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-but-2-en-1-ol (**7k**).* mp: 142−144 °C. IR (KBr): 3447 (−$OH_{aliphatic}$), 1225 (P═O), 757 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.26−6.61 (m, 7H, Ar−H), 5.15−4.97 (m, 2H, $-CH_2-$), 4.63 (s, 1H, *H*−C−OH), 3.06 (brs, 1H, H−C−O*H*), 5.20−4.85 (m, 2H, $-^aCH=^bCH-$), 1.28 (s, 3H, $-^cCH_3$). ^{13}C NMR (acetone-d_6): δ 43.68 (C-4), 129.49 (C-5), 120.29 (C-6), 128.82 (C-7), 117.56 (C-8), 157.23 (C-9), 128.55 (C-10), 141.57 (C-1′), 117.27 (C-2′), 120.29 (C-3′), 155.49 (C-4′), 115.94 (C-5′), 114.13 (C-6′), 118.12 (^{a}C), 134.92 (^{b}C), 21.32 (^{c}C), 61.93 (H−*C*−OH). ^{31}P NMR (acetone-d_6): δ −7.64. Anal. Calcd for $C_{17}H_{16}FClNO_3P$: C, 55.36; H, 4.61. Found: C, 55.31; H, 4.57.

Synthesis of 8a/b. Compound **7j/k** (0.01 mol) was dissolved in dichloromethane (30 mL). Hydrogen peroxide (30% H_2O_2, 0.01 mol) containing three drops of hexachloro acetone as a catalyst was added to it dropwise at 0−5 °C (*12*). The mixture was brought to room temperature and kept for 2 h. On completion of the reaction, as ascertained by TLC analysis, the compounds **8a** and **8b** were obtained in the pure state by column chromatography (**Scheme 2**).

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ⁵-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-3-phenyloxiranylmethanol (**8a**).* mp: 250−252 °C. IR (KBr): 3276 (−$OH_{aliphatic}$), 1262 (P═O), 750 cm^{-1} (P−$C_{aliphatic}$). ^1H NMR (acetone-d_6): δ 7.65−6.42 (m, 12H, Ar−H), 5.21−4.99 (m, 2H, $-CH_2-$), 4.52 (s, 1H, *H*−C−OH), 3.09 (brs, 1H,

Scheme 2 . Synthetic Scheme for Benzoxazaphosphinin-2-yl-(aryl/alkyl) oxiranylmethanol **8a/b**

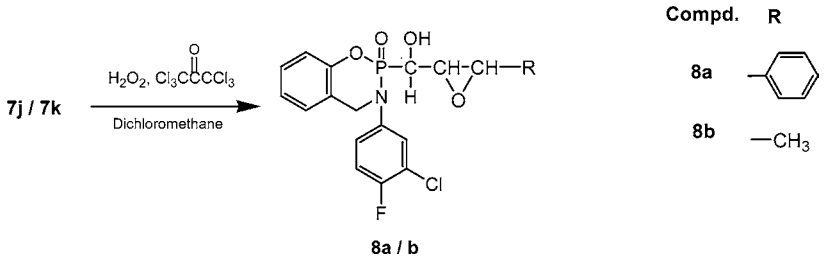

Table 2. Sensitivity of Spores of Smut of *Saccharum officinarum* to **7a**–**k** and **8a/b** in Slide Germination Technique[a]

	1000 ppm			750 ppm			500 ppm			250 ppm			100 ppm		
test compound	*C*	*T*	*P*	*C*	*T*	*P*	*C*	*T*	*P*	*C*	*T*	*P*	*C*	*T*	*P*
7a	100	0.0	100	100	0.0	100	100	0.0	100	100	18	82	100	44	56
7b	100	0.0	100	100	0.0	100	100	0.0	100	100	11	89	100	36	64
7c	100	0.0	100	100	0.0	100	100	0.0	100	100	13	87	100	32	68
7d	100	0.0	100	100	0.0	100	100	0.0	100	100	18	82	100	38	62
7e	100	0.0	100	100	0.0	100	100	0.0	100	100	17	83	100	42	58
7f	100	0.0	100	100	0.0	100	100	0.0	100	100	07	93	100	23	77
7g	100	0.0	100	100	0.0	100	100	0.0	100	100	05	95	100	19	81
7h	100	0.0	100	100	0.0	100	100	0.0	100	100	03	97	100	12	88
7i	100	0.0	100	100	0.0	100	100	0.0	100	100	08	92	100	27	73
7j	100	0.0	100	100	0.0	100	100	0.0	100	100	13	87	100	34	66
7k	100	0.0	100	100	0.0	100	100	0.0	100	100	10	90	100	37	63
8a	100	0.0	100	100	0.0	100	100	0.0	100	100	11	89	100	34	66
8b	100	0.0	100	100	0.0	100	100	0.0	100	100	08	92	100	39	61
bavistin	100	0.0	100	100	0.0	100	100	0.0	100	100	09	91	100	23	77

[a] C = number of spores germinated in the control; T = number of spores germinated in treatment; P = percentage inhibition over control [$C - T/C \times 100$].

H−C−O*H*), 5.36−5.16 (m, 2H, −epoxide−). ^{13}C NMR: Solubility was too low for recording. ^{31}P NMR (acetone-d_6): δ −4.33. FAB MS: *m*/*z* (%) 467 (7) [$M^{+\bullet}$+2], 465 (12) [$M^{+\bullet}$] , 463 (14), 369 (26), 327 (15), 281 (27), 252 (30), 212 (12), 124 (100). Anal. Calcd for $C_{22}H_{18}FClNO_4P$: C, 53.25; H, 4.42. Found: C, 53.32; H, 4.51.

*[3-(3-Chloro-4-fluorophenyl)-2-oxo-3,4-dihydro-2H-2λ^5-benzo[e]-[1,3,2]oxazaphosphinin-2-yl]-3-methyloxiranylmethanol (**8b**).* mp: 237−239 °C. IR (KBr): 3260 (−$OH_{aliphatic}$), 1222 (P═O), 756 cm^{-1} (P−$C_{aliphatic}$). ^{1}H NMR (acetone-d_6): δ 7.26−6.61 (m, 7H, Ar−H), 5.13−5.01 (m, 2H, −CH_2−), 4.63(s, 1H, *H*−C−OH), 3.18 (brs, 1H, H−C−O*H*), 4.63−4.38 (m, 2H, −epoxide−), 2.14−2.03 (m, 3H, CH_3). ^{13}C NMR: Solubility was too low for recording. ^{31}P NMR (acetone-d_6): δ −5.98. Anal. Calcd for $C_{17}H_{16}FClNO_4P$: C, 58.51; H, 3.61. Found: C, 58.62; H, 3.78.

Bioassays. Compounds **7a**−**k** and **8a**/**b** were tested for their bioactivity on whip smut of the sugarcane plant (*Saccharum officinarum*) and biodegradation in the environment and in the soil.

Effect on Smut of Sugarcane. Slide Germination Technique. A spore suspension was prepared from 10-day-old cultures of whip smut (*Ustilago scitaminea*). The spores were harvested with the help of a camel's hair brush by scraping over the culture and suspending the 10 mL of sterile distilled water in a test tube. The spore density was adjusted with distilled water so as to get 5.0×10^4 spores/mL with the help of a hemeocytometer (*13*).

Stock solutions of test compounds (**7a**−**k** and **8a**/**b**) and reference compound (bavistin) were prepared by dissolving required quantities in ethanol and diluting with 100 mL of sterile distilled water. Later test concentrations as given in the **Tables 2** and **3** were prepared by the serial dilution method.

The test and reference compounds containing 0.25 mL of test and reference solution, respectively, were placed in one of the two cavities of a microscopic cavity slide with the other cavity as a control. The solvent was allowed to evaporate, leaving a deposit of the test compound in the cavity of the slide. Equal quantities of the spore suspension were placed in cavities over the dried test compound. The cavities were covered with cover slips, and the slides were incubated in a moist chamber at 25 ± 2 °C for 24 h. The experiment was replicated three times, and control was maintained with distilled water in place of the test compound solution (**Table 2**).

Table 3. Percent of Inhibition by **7a**–**k** and **8a/b** on Smutted Shoot

test compound	1000 ppm	750 ppm	500 ppm	250 ppm	100 ppm	A	B
7a	100	100	97	92	83	0.0	0.0
7b	100	100	98	94	85	0.0	0.0
7c	100	100	100	96	88	0.0	0.0
7d	100	100	100	98	87	0.0	0.0
7e	100	100	100	97	87	0.0	0.0
7f	100	100	100	100	98	0.0	0.0
7g	100	100	100	100	97	0.0	0.0
7h	100	100	100	100	92	0.0	0.0
7i	100	100	100	100	94	0.0	0.0
7j	100	100	100	100	85	0.0	0.0
7k	100	100	100	100	91	0.0	0.0
8a	100	100	100	100	87	0.0	0.0
8b	100	100	100	100	95	0.0	0.0
bavistin	100	100	100	70	65	0.0	0.0

Effect of the Test Compound Treated on the Disease-Induced Plants. Exactly 15 pots were filled with sterile soil, and to each pot, a disinfected sugarcane stem piece, treated with formalin, was transferred and covered with a layer of soil in a greenhouse. For each treatment, 15 plants were treated. The pots were regularly watered to produce plants. Except for control "A" and control "B", all of the remaining 13 plants were treated with a test compound by foliar application at a specific quantity at recommended concentrations in an aqueous ethanol and water suspension. Later, after 2 days, control "B" and all the remaining treatments were sprayed with a smut spore suspension of *Ustilago scitaminea* to infect axillary buds through sporidia. The plants were observed for disease symptoms (*14*) from the 15th day to 60th day (**Table 3**).

Application on the Infected Plants. A total of 15 infected sugarcane plants that were 45 days old were selected in a farm enclosure for each treatment. Except for controls "A" and "B", all remaining 13 plants infected with *Ustilago scitaminea* were treated with a test compound by foliar application at a specific quantity at recommended concentrations (1000 ppm) in an aqueous ethanol and water suspension. For each

Table 4. Effect of **7a**–**k** and **8a/b** on the Number of Colonies of Phosphate Solubilizing Bacteria

T	7a	7b	7c	7d	7e	7f	7g	7h	7i	7j	7k	8a	8b	control
C	21.6	23.2	21.7	20.4	22.7	23.8	24.7	20.2	24.7	23.2	22.4	23	22.5	

T = test compound; C = total number of colonies of phosphate solubilizing bacteria.

Table 5. Number of Colony-Forming Units of Bacteria and Fungi by **7a**–**k** and **8a/b**

T	7a	7b	7c	7d	7e	7f	7g	7h	7i	7j	7k	8a	8b	calvixin
B	4060	4962	3645	3980	4140	5180	4780	6460	3280	3005	4890	5240	3870	2840
F	420	540	285	320	448	394	298	580	414	245	420	386	210	142

T = test compound; *B* = bacteria; *F* = fungi.

treatment, 15 plants were selected. Later, the plants were observed periodically for disease incidence (*14*) from the 4th day to 30th day.

Testing of Spore Germination. After the eighth day of treatment with test compounds, the spores of *Ustilago scitaminea* were collected from all of the above treated plants. The spore shapes were observed under the microscope, and their germination was artificially carried out by the method of Horsfall and Rich (*7*) with certain modifications. The treated and untreated spores were placed in two cavities of a microscopic cavity slide. The spore suspension prepared with sterile distilled water was adjusted to give 25−30 conidia of test organisms per 100 μL of spore suspension. Then, 100 μL of spore suspension was transferred on to each cavity of the microscopic slide. The cavities were covered with coverslips, and the slides were incubated in a moist chamber at 25 ± 2 °C for 24 h.

Phosphorus Transformation. (a) Colorimetric Method. Three test tubes, each containing 5 mL of distilled water, were taken and labeled as 1, 2, and 3. To test tubes 1 and 2 was added 1 mg of the test compound. To test tubes 1 and 3 was added an inoculums of phosphate solubilizing bacteria. After 7 days, the contents found in the three test tubes were filtered through bacterial filters and collected separately. The amount of soluble inorganic phosphates was measured by the colorimetric method (*15*) (**Table 4**). All the test compounds were screened in the same way.

(b) Dilution Plate Method. Soil samples from the sugarcane field were collected for the isolation of pesticide degrading/utilizing bacteria and fungi using the dilution plate method (*16*). The test compounds **7a**−**k** and **8a**/**b** were used to study the effect on the microbial population. Calixin, supplied by BASF-AG, Germany, was used as a reference compound. Soil extract agar and Czapek-Dox agar (*17*) amended with 100 ppm test compounds and Calixin were used for the enumeration of bacteria and fungi, respectively. Calixin-treated plates were considered as the control. The soil extract agar plates were incubated at 37 °C for bacterial growth, while the Czapek-Dox agar plates were incubated in an inverted position at room temperature (26 ± 2 °C) for fungal growth. The plates were observed regularly for the development of microbial colonies. On the basis of the colony morphology and microscopic observation, the bacterial and fungal species were identified, and the number of colony-forming units per gram of soil were calculated (**Table 5**).

RESULTS AND DISCUSSION

Synthesis. The addition of an equimolar amount of PBr_3 to **1** in dry toluene to obtain **2** depends on the temperature. If the reaction was carried out at room temperature, even after 8 h, some starting compound **1** remained in the reaction. At 50 °C, the reaction was completed in 3 h without leaving **1**. The preparation of **2** was carried out in the presence of a dry, inert atmosphere to prevent the early hydrolysis of the phosphorus bromides. It was observed that the hydrolysis of a P−Br bond was completed in a short time when compared to that of a P−Cl bond (*18*). The hydrolysis of a P−Br bond of **2** afforded P(III)−OH of **3**, which instantaneously rearranged into a more stable phosphoryl O═P(V)−H system (*19*). The hydrolysis should be done in the presence of triethylamine by the addition of a calculated quantity of water only. The addition of a little excess water led to an acid-catalyzed hydrolysis, giving the starting compound (**1**). The ease of addition of **4** to **5** and the percent yield of the products (**7a**−**k**) appeared to depend on the nature of the aldehyde. The addition of **4** to the arylaldehydes was completed in a short period of time, giving high yields of **7a**−**k** when compared to that of aliphatic aldehydes, which required more time (15−20 h) and gave poor yields. This could be due to the higher stability of the proposed intermediate **6** where greater delocalization of the electron density over the neighboring phosphoryl and aryl groups takes place. Furthermore, the overall reaction rate, the purity, and yield of the title compounds **7a**−**k** increased in the presence of a catalytic amount of Nb_2O_5 (**Table 1**). The mechanism and the role played by Nb_2O_5 is not known. Perhaps it may initially form an intermediate complex **6**, by reacting with **4** and activating the generation of the oxazaphosphinin-2-oxide anion **6** by catalyzing the selective partial deprotonation (*20*) of **4**. This consequently facilitates the formation of a P−C bond between the P of oxazaphosphinine (**4**) and the C of aldehyde **5**. The incorporation of Nb_2O_5 and Et_3N into the one face of the phosphorus nucleophile **6** enables it to discriminate the enantiotopic faces of the carbonyl carbon of the aldehyde and diastereoselectively add to it. Thus, the formation of only a single racemic compound of **7a**−**k** is favored. The presence of a single spot in TLC and one ^{31}P NMR chemical shift for **7a**−**k** confirmed this conclusion (*21*). Nb_2O_5 seems to have great potential as a chiral catalytic template that could mediate the stereochemistry of this addition. The synthesized compounds are characterized by elemental analysis; IR; ^{1}H, ^{13}C, and ^{31}P NMR; and mass spectral data (*22*, *23*).

7a−**k** and **8a**/**b** showed IR absorption bands in the regions 1262−1201, 768−729, and 3447−3069 cm^{-1} for P═O, $P-C_{(aliphatic)}$, and $(C)-O-H_{(aliphatic)}$, respectively (*24*). The aromatic protons of **7a**−**k** and **8a**/**b** resonated as multiplets slightly downfield (δ 8.72−6.49) when compared with those of the starting compound **1** (δ 7.20−7.49) owing to the deshielding effect of the benzoxazaphosphinin-2-oxide system. (*7*, *8*) The C-4 methylene protons exhibited a multiplet, indicating their non-equivalence and coupling with phosphorus in the six-membered ring (*8*). The aliphatic proton and the hydroxyl proton of H−C−OH gave signals in the regions δ 4.80−3.93 and δ 3.85−2.94, respectively (*18*). The ^{13}C NMR chemical shifts for C-4 to C-10, C-1 to C-6, and C-1″ to C-6″ were observed in the expected regions. The carbon signal of the aliphatic alcohol moiety appeared at δ 87.90−51.72 (*18*, *22*). The mass spectra of the representative compounds **7a**, **7b**,

7g, **7h**, **7i**, and **8a** were in accord with those reported for such types of organophosphorus compounds (*7*, *8*). They exhibited chlorine isotopic peaks at $(M+2)^+$. The M^+ peaks with the expected *m*/*z* value in the required ratio. The presence of characteristic ions with the benzoxazaphosphinin ring along with substituents at *m*/*z* 403, 327, 281, and 246 was in good agreement with the proposed structures.

Biological Activity. *Effect on Spore Germination.* The effect of the title compounds was initially tested in vitro by the slide germination test (*13*). After 24 h of incubation, a spore germination count was taken by using a compound microscope. The inhibition efficiencies of the test compounds were compared with inhibition efficiencies of the reference compound bavistin (carbendenzim). The results are shown in **Table 2**.

Drying of Whip Region. The encouraging results of the test compounds on the diseases infected plants induced us to carry out field-level studies (**Table 3**).

The plants treated with test compounds were found to be dried with splitting of the whip region when compared to those of the control. This type of effect was strongly observed in plants treated with test compounds **7f**, **7g**, **7h**, and **7i**. However, similar effects were not observed in the plants treated with bavistin supplied by BASF-India Ltd.

These results further revealed that these compounds not only cause the complete death and drying of the whip region of sugarcane plants but also promote the growth of the plants, simultaneously producing healthy side tillers in the clump without further infection. This indicated that the systemic spreading of the disease has been completely arrested in the plants treated with test compounds. Further, the test compounds prevented the secondary spread of the disease in the field to other healthy plants. These results are very encouraging when compared to the effect of Bavistin.

Spores Become Inactive. It was found that no single spore was germinated, when treated at 1000−250 ppm; moreover, the spores collected from plants treated with 100 ppm show a slight germination, but the germination was also found to be not healthy.

Interaction between Microorganisms and Test Compounds. The solution from test tube 1 was found to contain 20−25 μg of soluble inorganic phosphate, whereas tubes 2 and 3 were found to contain negligible or only traces of inorganic phosphates (**Table 4**). This shows that the molecules are easily degradable by microbial action to phosphate residues, which in turn may possibly act as nutrients for photosynthetic organisms (*25*).

Several bacterial and fungal species which can utilize organophosphate pesticide derivatives were isolated from soil in vitro. The fungal species like *Aspergillus flavus*, *Trichoderma harzianum*, and so forth and bacterial species like *Pseudomonas*, *Serratia micrococcus*, and so forth utilized the above pesticides as a phosphorus source and showed increased growth. The number of colony-forming units were greatest with compound **7h**, which indicated that this compound was more susceptible to and easily degradable by the microorganisms (**Table 5**). Hence, the results indicated that some of the microorganisms were able to degrade the title compounds to nutritive phosphate residues.

In summary, a simple and efficient synthesis is developed for the title compounds **7a**−**k** using Nb_2O_5 as a catalyst. Then, compounds are found to have a lethal effect on whip smut of sugarcane and at the same time acted as nutrients for the sugarcane plants. Furthermore, the test compounds are ecofriendly since they were degraded in the presence of some soil microbes to nontoxic phosphate residues.

ACKNOWLEDGMENT

The authors express their thanks to Dr. C. Naga Raju, Assistant Professor, Dept of Chemistry, S. V. University, Tirupati, India, for his helpful suggestions and to The Director, CDRI, Lucknow, India, for the analytical data.

Supporting Information Available: A detailed Scheme 1 giving full structures is given. The IR, ^{31}P, ^{1}H, ^{13}C, and FAB mass spectra of **7a** and its mass fragmentation are given as representative examples of this series. In addition, the ^{31}P spectrum of **7j** is also given. The color photographs of the effect of the test compounds **7f**, **7g**, **7h**, and **7i** on the smut of sugar cane and the healthy growth of the side tillers in the infected plants after the treatment are also given. The standard error of the mean for the assay values is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review March 22, 2007. Revised manuscript received June 14, 2007. Accepted June 22, 2007. One author (Y.B.K.) is grateful to UGC, New Delhi, for financial support.

JF070850Z