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Self-condensation reactions of acyl phosphonates: synthesis of tertiary *O*-protected α-hydroxyphosphonates

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In memory of Prof Dr Ayhan S Demir (1950–2012)

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Abstract: The self-condensation reaction of benzoyl dialkyl phosphonates was developed using cyanide ion as catalyst, affording versatile tertiary *O*-protected α-hydroxy phosphonates in moderate yield.

Key words: Acyl phosphonates, tertiary α-hydroxy phosphonates, phosphonate-phosphate rearrangement

1. Introduction

Hydroxy phosphonic acids and their ester derivatives have gained considerable attention due to their inhibitory activity towards various important groups of enzymes. For example, they have inhibitory effects on renin,[1,2] HIV protease,[3] farnesyl protein transferase,[4,5] (FPTase), and 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase.[6] Many hydroxy phosphonic acid derivatives have also been reported to have a broad range of biological activities such as antiviral,[7] antitumor,[8,9] and antibiotic properties.[10,11] Due to their biological activities, a great effort has been devoted to synthesize α-hydroxy phosphonates and derivatives in the last decade.[12–14] A variety of ways have been developed to obtain α-hydroxy phosphonates, such as phospho-aldol reaction,[15–20] reduction of α-keto phosphonates,[21–23] and oxidation of benzyl and vinyl phosphonates.[24,25] Although these methods are able to produce secondary α-hydroxy phosphonates, only a few methods have been described to synthesize tertiary α-hydroxy phosphonates. Wiemer et al. reported that the addition of allyl indium reagents to acyl phosphonates could provide tertiary α-hydroxy phosphonates.[26] The Zhao group reported the enantioselective synthesis of tertiary α-hydroxy phosphonates via aldol reaction.[27,28] Moreover, the Demir group reported the reaction of acyl phosphonates with trimethylsilyl cyanide to furnish the trimethylsilyloxycyanophosphonates.[29]

The Demir group and others have found that acyl phosphonates are new potent acyl anion precursors and undergo nucleophile-promoted phosphonate-phosphate rearrangement to afford the resultant acyl anion equivalents as reactive intermediates.[30–33] The proposed mechanism is similar to the benzoin reaction mechanism and its congeners. Cyanide ion-promoted rearrangement gives the acyl anion equivalent **3**, which reacts with aldehyde to provide the intermediate adduct **4**, undergoing a [1,4]-O,O-phosphate migration leading to retrocyanates to produce the corresponding benzoin product **6**.

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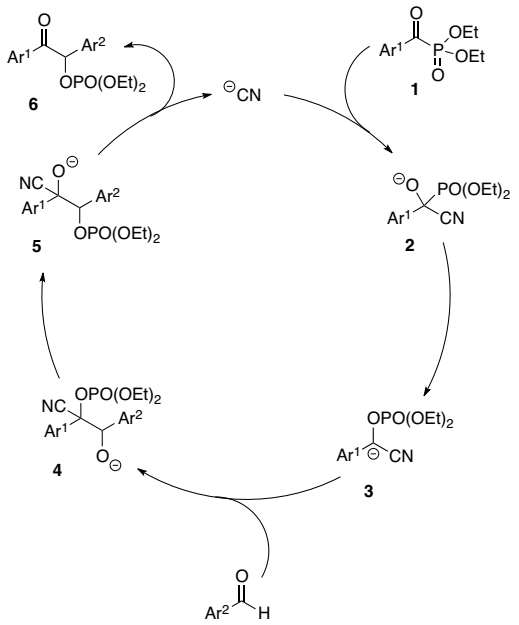
** Prof Dr Ayhan Sıtkı DEMİR passed away on 24 June 2012.

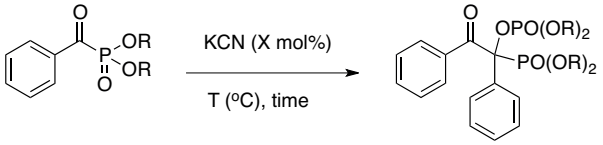


Scheme 1. Mechanism of cross-benzoin reaction via cyanide ion-promoted generation of acyl anions from acylphosphonates.

1.1. Results and discussion

As a general extension of earlier works,[30–33] we proposed that in the absence of an aldehyde the acyl anion equivalent generated from acyl phosphonate attacks another acyl phosphonate and produces *O*-protected tertiary α-hydroxy-phosphonates. As a model transformation the cyanide ion catalyzed self-condensation reaction of benzoyl dialkyl phosphonate was chosen. The results are summarized in Table 1.

Table 1. The optimization of reaction conditions for the synthesis of tertiary *O*-protected α-hydroxyphosphonates.



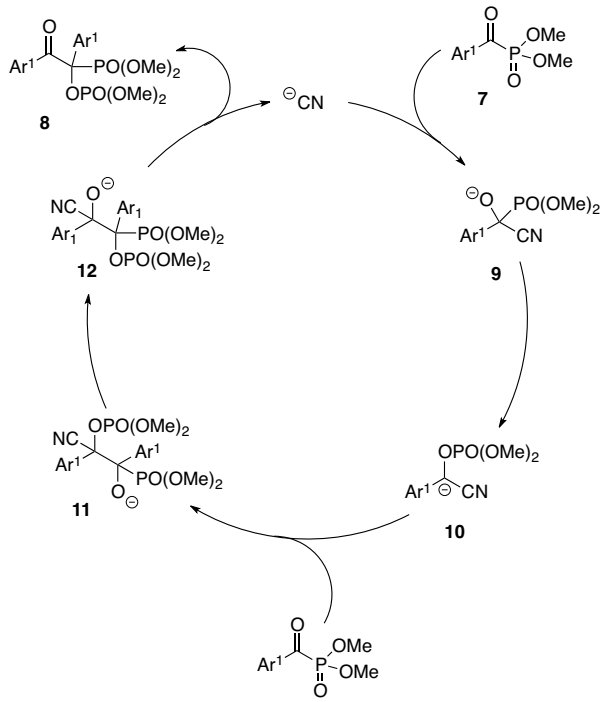
Entry	R	Solvent	KCN (mole %)	T (°C)	Time (h)	Yield (%)
1	Et	DMF	20	25	48	40
2	Et	THF	20	25	72	25
3	Et	THF	30	25	72	36
4	Et	DMF	30	25	48	42
5	Et	DMF	30	40	48	50
6	Me	DMF	20	25	48	46
7	Me	THF	30	25	72	44
8	Me	DMF	20	40	24	52
9	Me	DMF	20	75	24	56
10	Me	DMF	30	75	24	62

As can be seen in Table 1, the initial results showed that the cyanide ion effectively catalyzed the self-condensation reaction of acyl phosphonates. Reaction times ranged from 24 to 72 h at 25–75 °C. The use of KCN in DMF was successful. Poorer reactivity was observed in THF. Increasing the catalyst loading caused

a slight increase in yield (Table 1, entry 2). Benzoyl dimethyl phosphonate gave a higher yield than benzoyl diethyl phosphonate (Table 1, entry 6). The higher loading of the cyanide as a catalyst led to a higher yield of the product. At 40 °C and 75 °C, the products were obtained in 52% and 55% yield, respectively (Table 1, entry 5). Moreover, at these temperatures, the reaction time was shortened. Finally, acceptable yields were obtained at 75 °C with 30% mole KCN (Table 1, entry 10).

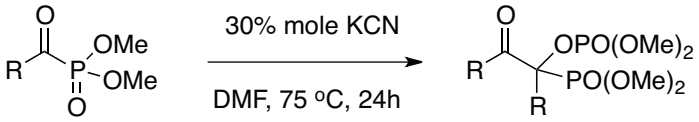
With these optimized reaction conditions in hand, we then examined the scope of the corresponding reaction with different benzoyl dimethylphosphonates. As shown in Table 2, the reaction proceeded smoothly and was completed in 24 h with isolated yields ranging from 45% to 65%. It should be stated that all examples engaged aryl-substituted keto phosphonates (aryl phosphonates). Electron-rich, -poor, and -neutral aryl phosphonates were well tolerated. 4-Methoxy and 4-methyl benzoyl dimethylphosphonates furnished the reaction in good yields (65% and 60% yield, respectively, Table 2, entries 2 and 3). On the other hand, 4-fluoro benzoyl dimethylphosphonate gave only 45% yield (Table 2, entry 4). Meta-substituted aryl phosphonates also gave good yields (Table 2, entries 6 and 7). The main difficulty encountered with this reaction is the reaction of ortho-substituted aryl phosphonates and also alkyl phosphonates. No product formation was detected when ortho-substituted aryl phosphonates were employed (Table 2, entry 9). Alkyl phosphonates also gave no reaction. The structures of the corresponding products were established from their spectral (^{1}H, ^{13}C, and ^{31}P NMR) and analytical data.

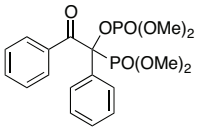
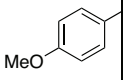
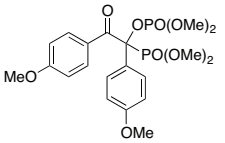
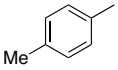
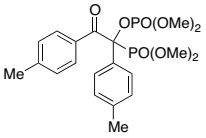
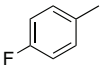
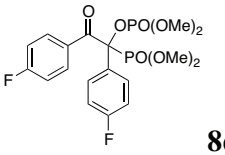
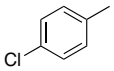
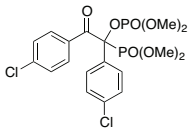
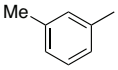
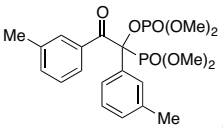
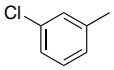
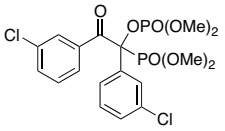
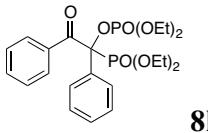
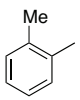
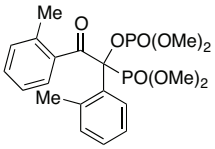
The proposed catalytic cycle for the formation of O-protected α-hydroxy phosphonates is based on the classical route of benzoin condensation, which has common key steps for a variety of congeners of this reaction like acylphosphonates (Scheme 2). In this context, acyl anion intermediate **10** generated from cyanide ion promoted rearrangement reacts with another acyl phosphonate to afford intermediate **11**, which undergoes a 1,4-phosphate migration yielding tertiary $O-$protected α-hydroxy phosphonate **8**.



Scheme 2. Proposed mechanism for $O-$protected α-hydroxy phosphonate formation.

Table 2. Scope of the reaction with derivatives of benzoyl dimethylphosphonates.



Entry	R	Product	Yield (%)
1		 **8a**	62
2		 **8b**	65
3		 **8c**	60
4		 **8d**	45
5		 **8e**	50
6		 **8f**	59
7		 **8g**	61
8[a]		 **8h**	54
9		 **8i**	nd

[a]benzoyl dimethylphosphonate was used

In conclusion, we have described a new method for the synthesis of $O-$protected α-hydroxy phosphonates. This method works well with aryl-substituted keto phosphonates. The cyanide ion catalyzed formation of acyl anion from aryl phosphonates and the reaction of this anion with another aryl phosphonates furnished corresponding O-protected α-hydroxy phosphonates in 42%–65% yields.

2. Experimental section

2.1. General

All commercially available reagents were used without further purification. DMF was purified by distillation under vacuum and stored over 4-Å molecular sieves. Purification of the products was carried out by flash column chromatography using silica gel 60. Analytical thin layer chromatography was performed on aluminum sheets precoated with silica gel 60F254. ^{1}H, ^{13}C, and ^{31}P NMR spectra were reported on a Bruker Spectrospin Avance DPX-400 Ultrashield instrument at 400, 100, and 162 MHz, respectively, relative to TMS for ^{1}H and ^{13}C NMR and H_3PO_4 for ^{31}P NMR. Data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration. Elemental analyses were conducted at the METU Central Laboratory using a LECO, CHNS-932.

2.2. General experimental procedure for the preparation of O-protected α-hydroxy phosphonates

First 13 mg of KCN was dried at 100 °C under vacuum for 3 h and dissolved in dry DMF (1 mL). Then 1 mmol of acyl phosphonate was added. The reaction mixture was stirred under argon atmosphere for 24 h at 75 °C. The reaction was diluted with Et_2O and brine solution was added. The aqueous phase was extracted with Et_2O 3 times. The collected organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel with EtOAc as eluent.

2.3. 1-(Methoxyphosphono)-2-oxo-1,2-diphenylethyl dimethyl phosphate (8a)

Yield: 62%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 3.29 (d, J = 11.5 Hz, 3H); 3.67 (d, J = 10.8 Hz, 3H); 3.73 (d, J = 11.6 Hz, 3H); 3.79 (d, J = 10.9 Hz, 3H); 7.16–7.20 (m, 3H); 7.30–7.36 (m, 3H); 7.52 (d, J = 7.2 Hz, 2H); 7.61 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) 53.2 (d, J = 7.1 Hz); 53.4 (d, J = 6.1 Hz); 53.7 (d, J = 6.6 Hz); 54.0 (d, J = 6.1 Hz); 90.2; 126.3 (d, J = 3.6 Hz); 127.8; 128.4; 128.6 (d, J = 2.7 Hz); 130.5; 132.5; 134.3 (d, J = 4.5 Hz); 134.8 (d, J = 7.1 Hz); 192.7; ^{31}P NMR ($CDCl_3$) –5.62; 12.70. $C_{18}H_{22}O_8P_2$ (428.08): Calcd C, 50.48; H, 5.18; O, 29.88; P, 14.46; found C, 50.42; H, 5.01; O, 30.10; P, 14.50.

2.4. 1-(Methoxyphosphono)-1,2-bis(4-methoxyphenyl)-2-oxoethyl dimethyl phosphate (8b)

Yield: 65%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 3.40 (d, J = 11.5 Hz, 3H); 3.68 (d, J = 10.7 Hz, 3H); 3.71 (s, 3H); 3.72 (d, J = 11.1 Hz, 3H); 3.73 (s, 3H); 3.77 (d, J = 10.9 Hz, 3H); 6.68 (d, J = 8.9 Hz, 2H); 6.83 (d, J = 8.8 Hz, 2H); 7.41 (dd, J_1 = 2.2 Hz, J_2 = 8.9 Hz, 2H); 7.66 (d, J = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) 53.1 (d, J = 7.4 Hz); 53.3 (d, J = 6.0 Hz); 53.8 (d, J = 7.3 Hz); 54.1 (d, J = 6.1 Hz); 54.2; 54.3; 12.3; 113.0; 125.1; 125.8 (d, J = 6.2 Hz); 126.8 (d, J = 4.2 Hz); 132.0; 159.0 (d, J = 2.8 Hz); 162.2; 190.6; ^{31}P NMR ($CDCl_3$) –2.86; 15.9. $C_{20}H_{26}O_{10}P_2$ (488.10): Calcd C, 49.19; H, 5.37; O, 32.76; P, 12.68; found C, 49.02; H, 5.45; O, 33.15; P, 12.57.

2.5. 1-(Methoxyphosphono)-2-oxo-1,2-bis-tolylethyl dimethyl phosphate (8c)

Yield: 60%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 2.22 (s, 3H); 2.27 (s, 3H); 3.36 (d, J = 11.5 Hz, 3H); 3.67 (d, J = 10.8 Hz, 3H); 3.72 (d, J = 11.6 Hz, 3H); 3.77 (d, J = 10.9 Hz, 3H); 6.99 (d, J = 8.1 Hz, 2H); 7.12 (d, J = 8.0 Hz, 2H); 7.37 (d, J = 8.2 Hz, 2H); 7.54 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) 20.1; 20.6; 53.1 (d, J = 7.0 Hz); 53.3 (d, J = 6.0 Hz); 53.8 (d, J = 6.5 Hz); 54.1 (d, J = 6.2 Hz); 59.3; 125.1 (d, J = 4.2 Hz); 126.8; 127.0; 127.67; 128.2 (d, J = 2.7 Hz); 129.6, 130.5; 130.6; 191.8; ^{31}P NMR ($CDCl_3$) –3.35; 15.69. $C_{20}H_{26}O_8P_2$ (456.11): calcd C, 52.64; H, 5.74; O, 28.05; P, 13.57; found C, 52.56; H, 5.67; O, 28.85; P, 13.50.

2.6. 1-(Methoxyphosphono)-1,2-bis(4-fluorophenyl)-2-oxoethyl dimethyl phosphate (8d)

Yield: 45%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 3.38 (d, J = 11.5 Hz, 3H); 3.68 (d, J = 10.8 Hz, 3H); 3.75 (d, J = 11.6 Hz, 3H); 3.80 (d, J= 10.9 Hz, 3H); 6.89 (d, J = 8.6 Hz, 2H); 7.03 (d, J = 8.5 Hz, 2H); 7.47–7.51 (m, 2H); 7.66 (dd, J_1 = 8.7 Hz, J_2 = 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) 54.31 (d, J = 6.0 Hz); 55.23 (J = 6.2 Hz); 60.45; 115.18; 115.40; 115.78; 115.98; 128.31; 130.26; 133.16; 133.25; 191.44; ^{31}P NMR ($CDCl_3$) –3.15; 15.02. $C_{18}H_{20}F_2O_8P_2$ (464.06): calcd C, 46.56; H, 4.34; F, 8.18; O, 27.57; P, 13.34; found C, 47.03; H, 4.45; F, 8.11; O, 28.02; P, 13.29.

2.7. 1-(Methoxyphosphono)-1,2-bis(4-chlorophenyl)-2-oxoethyl dimethyl phosphate (8e)

Yield: 50%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 3.38 (d, J = 11.5 Hz, 3H); 3.69 (d, J = 10.9 Hz, 3H); 3.76 (d, J = 11.6 Hz, 3H); 3.81 (d, J= 10.9 Hz, 3H); 7.19 (d, J = 8.7 Hz, 2H); 7.31 (d, J = 8.6 Hz, 2H); 7.41 (dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz 2H); 7.56 (dd, J_1 = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) 54.3 (d, J = 3.2 Hz); 54.4 (d, J = 2.8 Hz); 55.6 (d, J = 1.7 Hz); 55.7 (d, J = 1.1 Hz); 96.1; 127.1 (d, J = 4.4 Hz); 127.5 (d, J = 4.4 Hz); 128.5; 128.6; 128.8; 129.1 (d, J = 5.6 Hz); 131.5; 131.8 (d, J = 4.5 Hz); 192.8; ^{31}P NMR ($CDCl_3$) –2.80; 15.27. $C_{18}H_{20}Cl_2O_8P_2$ (496.00): calcd C, 43.48; H, 4.05; Cl, 14.26; O, 25.74; P, 12.46; found C, 43.45; H, 4.25; Cl, 14.32; O, 26.14; P, 12.40.

2.8. 1-(Methoxyphosphono)-2-oxo-1,2-di-*m*-tolylethyl dimethyl phosphate (8f)

Yield: 59%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 2.22 (s, 3H); 2.29 (s, 3H); 3.28 (d, J = 11.5 Hz, 3H); 3.66 (d, J = 10.8 Hz, 3H); 3.73 (d, J = 11.6 Hz, 3H); 3.78 (d, J = 10.9 Hz, 3H); 7.00–7.33 (m, 7H); 7.55 (s, 1H); ^{13}C NMR ($CDCl_3$) 20.3; 20.6; 52.9 (d, J = 6.5 Hz); 53.0 (d, J = 5.8 Hz); 53.8 (d, J = 6.3 Hz); 53.9 (d, J = 6.2 Hz); 89.6; 122.2 (d, J = 3.8 Hz); 125.7 (d, J = 4.2 Hz); 126.5; 126.7; 127.4 (d, J = 2.6 Hz); 128.7 (d, J = 2.6 Hz); 130.1; 132.5; 132.8 (d, J = 4.4 Hz); 133.3 (d, J = 6.9 Hz); 136.7; 137.1 (d, J = 2.7 Hz); 191.2; ^{31}P NMR ($CDCl_3$) –3.12; 15.56. $C_{20}H_{26}O_8P_2$ (456.11): calcd C, 52.64; H, 5.74; O, 28.05; P, 13.57; found C, 52.60; H, 5.70; O, 28.55; P, 13.51.

2.9. 1-(Methoxyphosphono)-1,2-bis(3-chlorophenyl)-2-oxoethyl dimethyl phosphate (8g)

Yield: 61%; colorless oil; ^{1}H NMR ($CDCl_3$)δ 3.38 (d, J = 11.5 Hz, 3H); 3.71 (d, J = 10.9 Hz, 3H); 3.78 (d, J = 11.6 Hz, 3H); 3.82 (d, J= 10.9 Hz, 3H); 7.24–7.37 (m, 5H); 7.47 (td, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1H); 7.53–7.55 (m, 1H); 7.64 (t, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$); 54.5 (d, J = 4.5 Hz); 54.7 (d, J = 2.2 Hz); 55.5 (d, J = 6.7 Hz); 55.7 (d, J = 6.2 Hz); 96.4; 124.7 (d; J = 4.5 Hz); 125.6 (d, J = 2.2 Hz); 126.3 (d, J

= 4.0 Hz); 128.7; 129.7; 129.8 (d, J = 3.0 Hz); 130.3 (d, J = 2.6 Hz); 130.6; 133.4; 134.7; 192.9; ^{31}P NMR ($CDCl_3$) –2.43; 15.10. $C_{18}H_{20}Cl_2O_8P_2$ (496.00): calcd C, 43.48; H, 4.05; Cl, 14.26; O, 25.74; P, 12.46; found C, 43.54; H, 4.16; Cl, 14.30; O, 26.15; P, 12.38.

2.10. 1-(Ethoxyphosphono)-2-oxo-1,2-diphenylethyl diethyl phosphate (8h)

Yield: 54%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, J = 7.0 Hz, 3H); 1.17 (t, J = 7.0 Hz, 3H); 1.19–1.26 (m, 6H); 3.50–3.66 (m, 2H); 3.93–4.22 (m, 6H); 7.13–7.19 (m, 3H); 7.25–7.35 (m, 3H); 7.50 (d, J = 7.2 Hz); 7.58 (d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) 15.8 (d, J = 8.2 Hz); 16.0 (d, J = 8.4 Hz); 16.3 (d, J = 5.7 Hz); 16.4 (d, J = 6.5 Hz); 63.3 (d, J = 7.4 Hz); 63.5 (d, J = 5.8 Hz); 64.1 (d, J = 7.8 Hz); 64.3 (d, J = 7.2 Hz); 90.4; 126.5 (d, J = 3.7 Hz); 127.7; 128.3; 128.7 (d, J = 2.8 Hz); 130.6; 132.4; 134.4 (d, J = 4.5 Hz); 134.7 (d, J = 7.2 Hz); 192.9; ^{31}P NMR ($CDCl_3$) –5.58; 12.64. $C_{18}H_{22}O_8P_2$ (428.08): calcd C, 50.48; H, 5.18; O, 29.88; P, 14.46; found C, 50.55; H, 5.23; O, 30.11; P, 14.40.

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References

1. Dellaria, J. F., Jr.; Maki, R. G.; Stein, H. H.; Cohen, J.; Whittern, D.; Marsh, K.; Hoffman, D. J.; Plattner, J. J.; Perun, T. J. *J. Med. Chem.* **1990**, *33*, 534–542.
2. Tao, M.; Bihovsky, R.; Wells, G. J.; Mallamo, J. P. *J. Med. Chem.* **1998**, *41*, 3912–3916.
3. Stowasser, B.; Budt, K. H.; Jian-Qi, L.; Peyman, A.; Ruppert, D. *Tetrahedron Lett.* **1992**, *33*, 6625–6628.
4. Pompliano, D. L.; Rands, E.; Schaber, M. D.; Mosser, S. D.; Anthony, N. J.; Gibbs, J. B. *Biochemistry* **1992**, *31*, 3800–3807.
5. Hohl, R. J.; Lewis, K. A.; Cermak, D. M.; Wiemer, D. F. *Lipids* **1998**, *33*, 39–46.
6. Sikorski, J. A.; Miller, M. J.; Braccolino, D. S.; Cleary, D. G.; Corey, S. D.; Font, J. L.; Gruys, K. J.; Han, C. Y.; Lin, K. C.; Pansegrau, P. D.; et al. *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *76*, 115–117.
7. Snoeck, R.; Holy, A.; Dewolf-Peeters, C.; Van Den Oord, J.; De Clercq, E.; Andrei, G. *Antimicrob. Agents Chemother.* **2002**, *46*, 3356–3361.
8. Peters, M. L.; Leonard, M.; Licata, A. A. *Clev. Clin. J. Med.* **2001**, *68*, 945–951.
9. Leder, B. Z.; Kronenberg, H. M. *Gastroenterology* **2000**, *119*, 866–869.
10. Huber, J. W.; Gilmore, W. F.; Robertson, L. W.; *J. Med. Chem.* **1975**, *18*, 106–108.
11. Atherton, F. R.; Hall, M. J.; Hassall, C. H.; Holmes, S.W.; Lambert, R.W.; Lloyd, J.; Ringrose, P. S. *Antimicrob. Agents Chemother.* **1980**, *18*, 897–905.
12. Kolodiazhnyi, O. I. *Tetrahedron: Asymmetry* **1998**, *9*, 1279–13332.
13. Kolodiazhnyi, O. I. *Advances in Asymmetric Synthesis Vol. 3*, JAI Press: London, 1998, 273.
14. Kolodiazhnyi, O. I. *Russian Chemical Reviews* **2006**, *75*, 227–253.
15. Engel, R. *Synthesis of Carbon–Phosphorus Bonds*, CRC Press: Boca Raton, FL, 1987.
16. Yokomatsu, T.; Yamagishi, T.; Shibuya, S. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1527–1533.
17. Wroblewski, A. E.; Balcerzak, K. B. *Tetrahedron: Asymmetry* **2001**, *12*, 427–431.
18. Yokomatsu, T.; Yamagishi, T.; Shibuya, S. *Tetrahedron: Asymmetry* **1993**, *4*, 1401–1404.

19. Rowe, B. J.; Spilling, C. D. *Tetrahedron: Asymmetry* **2001**, *12*, 1701–1708.
20. Arai, T.; Bougauchi, M.; Sasai, H.; Shibasaki, M. *J. Org. Chem.* **1996**, *61*, 2926–2927.
21. Gajda, T. *Tetrahedron: Asymmetry* **1994**, *5*, 1965–1972.
22. Nesterov, V. V.; Kolodiazhnyi, O. I. *Zh. Obshch. Khim.* **2005**, *75*, 1225–1229.
23. Meier, C.; Laux, W. H. G. *Tetrahedron: Asymmetry* **1996**, *7*, 89–94.
24. Pogatchnik, D. M.; Wiemer, D. F. *Tetrahedron Lett.* **1997**, *38*, 3495–3498.
25. Yokomatsu, T.; Yamagishi, T.; Suemune, K.; Yoshida, Y.; Shibuya, S. *Tetrahedron* **1998**, *54*, 767–780.
26. Wiemer, D. F.; Kim, D. Y. *Tetrahedron Lett.* **2003**, *44*, 2803–2805.
27. Samanta, S.; Zhao, C.-G. *J. Am. Chem. Soc.* **2006**, *128*, 7442–7443.
28. Perera, S.; Naganaboina, V. K.; Wang, L.; Zhang, B.; Guo, Q.; Rout, L.; Zhao, C.-G. *Adv. Synth. Catal.* **2011**, *10*, 1729–1734.
29. Demir, A. S.; Reis, Ö.; Kayalar, M.; Eymur, S.; Reis, B. *Synlett* **2006**, *19*, 3329–3333.
30. Demir, A. S.; Reis, Ö.; İgdir, A. Ç.; Esiringü, İ.; Eymur, S. *J. Org. Chem.* **2005**, *70*, 10584–10587.
31. Demir, A. S.; Reis, Ö.; Esiringü, I.; Reis, B.; Baris, S. *Tetrahedron* **2007**, *63*, 160–165.
32. Demir, A. S.; Reis, B.; Reis, Ö.; Eymur, S.; Göllü, M.; Tural, S.; Saglam, G. *J. Org. Chem.* **2007**, *72*, 7439–7442.
33. Demir, A. S.; Eymur, S. *J. Org. Chem.* **2007**, *72*, 8527–8530.