Supporting Information

A Facile Route to Vinyl- and ArylPhosphonates by Vinyl and Aryl**Radical Trapping with (MeO)₃P**

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Dimethyl (*E*)-1-Methyl-1-propenylphosphonate¹⁴ (Table 1, entry 1) was prepared by thermal AIBN/*n*-Bu₃SnH method described for the other entries of Table 1. Chromatography on silica gel (eluent, ethyl acetate) gave the product as a colorless oil, 83% yield (*E* and *Z*- isomers). When *tris*-(trimethylsilyl)silane was used in the same molar amount in place of tri-*n*-butyltin hydride (Tables 2 and 3)), the product yield was 70% (*E/Z* ratio 70/30). The individual diastereomers were separated by flash chromatography on silica gel (ethyl acetate) though yield were not determined. ¹H NMR (500 MHz, CDCl₃): δ 1.77 (ddq, *J*_{PH} = 14.8 Hz, *J* = 1.65, 1.1 Hz, 3 H), 1.80 (ddq, *J*_{PH} = 3.6 Hz, *J* = 6.8, 1.1 Hz, 3 H), 3.71 (d, *J*_{PH} = 11.0 Hz, 6 H), 6.66 (dq, *J*_{PH} = 23.5 Hz, *J* = 6.8, 1.65 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 12.24 (d, *J*_{PC} = 11.0 Hz), 14.38 (d, *J*_{PC} = 20.8 Hz), 52.28 (d, *J*_{PC} = 5.5 Hz), 124.27 (d, *J*_{PC} = 180.4 Hz), 142.47 (d, *J*_{PC} = 10.9 Hz). ³¹P NMR (121 MHz, CDCl₃): δ 25.1; HRMS (EI) C₆H₁₃O₃P (M⁺) found 164.06048, calcd 164.06023, Δ*m*, -0.25 mu. **Dimethyl (*Z*)-1-Methyl-1-propenylphosphonate**.¹⁴ ¹H NMR (300 MHz, CDCl₃): δ 1.88 (ddq, *J*_{PH} = 13.0 Hz, *J* = 1.5, 1.5 Hz, 3 H), 2.04 (ddq, *J*_{PH} = 3.6 Hz, *J* = 1.5, 7.3 Hz, 3 H), 3.72 (d, *J*_{PH} = 11.2 Hz, 6 H), 6.34 (dq, *J*_{PH} = 50.8 Hz, *J* = 7.3, 1.5 Hz, 1 H). ¹³C NMR (125 MHz, CDCl₃): δ 16.42 (d, *J*_{PC} = 7.3 Hz), 21.85 (d, *J*_{PC} = 12.6 Hz), 52.05 (d, *J*_{PC} = 5.7 Hz), 123.83 (d, *J*_{PC} = 172.8 Hz), 143.89 (d, *J*_{PC} = 12.2 Hz). ³¹P NMR (121 MHz, CDCl₃): δ 22.7; HRMS (EI) C₆H₁₃O₃P (M⁺) found 164.06027, calcd 164.06023, Δ*m*, -0.04 mu.

Dimethyl 2-Methyl-1-propenylphosphonate¹⁵ (Table 1, entry 5) was prepared by the thermal AIBN/*n*-Bu₃SnH approach. Chromatography on silica gel column (eluent, ethyl acetate) gave the product as a colorless oil, 81% yield. When tris-(trimethylsilyl)silane was in the same molar amount in place of tri-*n*-butyltin hydride, the isolated yield of the reaction was 84%. ¹H NMR (300 MHz, CDCl₃): δ 1.94 (dd, *J* = 1.2, 1.2 Hz, 3 H), 2.10 (dd, *J*_{PH} = 3.2 Hz, *J* = 1.2 Hz, 3 H), 3.71 (d, *J*_{PH} = 11.1 Hz, 6 H), 5.37 (dq, *J*_{PH} = 19.2 Hz, *J* = 1.2, 1.2 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 21.73 (d, *J*_{PC} = 6.7 Hz), 28.46 (d, *J*_{PC} = 24.7 Hz), 52.06 (d, *J*_{PC} = 5.4 Hz), 110.95 (d, *J*_{PC} = 189.5 Hz), 160.88 (d, *J*_{PC} = 6.4 Hz); ³¹P NMR (121 MHz, CDCl₃): δ 21.3; Anal. Calcd for C₆H₁₃O₃P: C, 43.90; H, 7.98. Found: C, 43.93; H, 8.03.

Dimethyl 4-Trifluoromethylphenylphosphonate (Table 2, entry 8) was prepared by the thermal AIBN/*n*-Bu₃SnH approach 80 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.76 (d, *J*_{PH} = 11.1 Hz, 3 H), 3.77 (d, *J*_{PH} = 10.8 Hz, 3 H), 7.69-7.74 (m, 2 H), 7.88-7.95 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ 53.10 (d, *J*_{PC} = 5.5 Hz), 123.67 (q, *J*_{FC} = 272.79 Hz), 125.58 (dq, *J*_{FC} = 15.3 Hz, 3.7 Hz), 131.51 (d, *J*_{PC} = 186.6 Hz), 132.57 (d, *J*_{PC} = 10.0 Hz), 134.47 (dq, *J*_{FC} = 29.3 Hz, *J*_{PC} = 4.4 Hz); ³¹P NMR (121 MHz, CDCl₃): δ 19.5; Anal. Calcd for C₉H₁₀F₃O₃P: C, 42.53; H, 3.97. Found: C, 42.59; H, 4.17.

References

1. Gareev, R. D.; Chernova, A. V.; Ishmaeva, E. A.; Berdnikov, E.; A.; Shagidullin, R.; Strelkova, E. N.; Dorozhkina, G. M.; Patsanovskii, I. I. and Pudovik, A. N. *Zh. Obshch. Khim.* **1982**, 52, 2444.
2. Marmor, R. S. and Seyforth, D. *J. Org. Chem.* **1971**, 36, 128.

Jiao3-86, H

jiao3-86,C
jiao3-86,C

exp6 std13c

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 at 1.814 dmf undefined
 np 72576 dseq undefined
 sw 20000.0 dres undefined
 fb 11000 homo n
 bs 16 PROCESSING
 tpwr 49 lb 1.00
 pw 16.0 wtfile
 dl 0 proc ft
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 nt 20000 math
 ct 32
 alock n werr
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 hs nn
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jiao3-86,C
jiao3-86,C

exp6 std13c

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alock	n	warr	
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dp	n		
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