Self-Protection: The Advantage of Radical Oligomeric Mixtures in Organic Synthesis

Hui Yu and Chaozhong Li*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai

200032, P. R. China

clig@mail.sioc.ac.cn

Supporting Information

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NMR spectra were recorded in CDCl₃ (¹H at 300 MHz and ¹³C at 75.47 MHz) using TMS as the internal standard. The melting points were uncorrected. All products were isolated by column chromatography on silica gel with hexane - ethyl acetate in an appropriate ratio as the eluent. Methylene chloride was dried over CaH₂ and freshly distilled prior to use. THF was refluxed with Na and distilled prior to use. Triethylborane (1 M solution in hexane) was commercially available and used without further purification.

Substrates **1**, **7-10**, **15-18** were prepared according to the conventional methods.¹

Compounds **1**,² **7**,³ **8**,⁴ **9**,⁵ **15**,¹ **16**,⁶ **17**,⁶ **18**³ had the same spectra as in the literature.

1-Hepten-3-yl iodoacetate (10). Colorless liquid. B.p. 78-80°C/1 mmHg. ¹H NMR (300 MHz, CDCl₃) δ 0.80-0.85 (3H, t, *J* = 6.9 Hz), 1.19-1.30 (4H, m), 1.50-1.63 (2H, m), 3.61 (2H, s), 5.10-5.25 (3H, m), 5.65-5.76 (1H, m). EIMS: *m/z* (rel intensity) 282 (M⁺, 1), 169 (100), 155 (57), 95 (63), 69 (35), 55 (90), 42 (35), 41 (56). Anal. calcd for C₉H₁₅IO₂: C, 38.32; H, 5.36. Found: C, 38.32; H, 5.39.

The spectra of compounds **10a**,⁷ **10b**,⁸ **10c**,⁹ **10d**¹⁰ and **10e**¹¹ synthesized were identical with those reported in the literature.

2,2-Diphenyl-5-(2-hydroxyethyl)tetrahydrofuran (14b). White solid. M.p. 85-86°C. ¹H NMR (300 MHz, CDCl₃) δ 1.71-2.11 (4H, m), 2.51-2.60 (1H, m), 2.64-2.73 (1H, m), 2.92 (1H, br), 3.86-3.91 (2H, m), 4.28-4.35 (1H, m), 7.17-7.46 (10H, m). ¹³C NMR (CDCl₃) δ 31.7, 38.1, 38.5, 61.8, 79.1, 88.8, 125.7, 125.8, 126.7, 128.1, 128.2, 145.8, 146.4. EIMS: *m/z* (rel intensity) 268 (M⁺, 10), 250 (3), 191 (91), 115 (14), 105 (100), 77 (34). Anal. calcd for C₁₈H₂₀O₂: C, 80.56; H, 7.51. Found: C, 80.21; H, 7.60.

2,2-Di(2-propenyl)-5-(2-hydroxyethyl)tetrahydrofuran (14c). Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.55-1.67 (1H, m), 1.73-1.84 (4H, m), 1.96-2.05 (1H, m), 2.21-2.29 (4H, m), 3.07 (1H, t, *J* = 4.5 Hz), 3.77 (2H, dd, *J* = 9.6, 4.5 Hz), 4.07-4.15 (1H, m), 5.04-5.09 (4H, m), 5.74-5.89 (2H, m). ¹³C

NMR (CDCl₃) δ 32.1, 33.5, 37.4, 43.6, 44.3, 61.6, 79.4, 85.0, 117.7, 117.8, 134.1, 134.2. EIMS: m/z (rel intensity) 155 (91), 125 (15), 95 (16), 69 (96), 55 (41). Anal. calcd for C₁₂H₂₀O₂: C, 73.43; H, 10.27. Found: C, 73.11; H, 10.24.

2,2-Dimethyl-5-(2-hydroxyethyl)tetrahydrofuran (14d). Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.23 (3H, s), 1.26 (3H, s), 1.68-1.80 (5H, m), 2.04-2.09 (1H, m), 3.21 (1H, br), 3.77 (2H, t, J = 5.1 Hz), 4.14-4.18 (1H, m). ¹³C NMR (CDCl₃) δ 28.0, 29.2, 32.0, 37.9, 38.0, 61.5, 78.7, 81.3. EIMS: m/z (rel intensity) 144 (M⁺, 2), 129 (25), 111 (7), 99 (55), 81 (52), 43 (100). HRMS calcd for C₇H₁₃O₃ (M⁺-CH₃); 129.0914. Found: 129.0927.

2,2-Diphenyl-5-(3-hydroxypropyl)tetrahydrofuran (14e). White solid. M.p 67-68°C. ¹H NMR (300 MHz, CDCl₃) δ 1.64-1.78 (5H, m), 2.01-2.07 (1H, m), 2.38 (1H, br), 2.53-2.69 (2H, m), 3.73 (2H, br), 4.13-4.17 (1H, m), 71.6-7.41 (10H, m). ¹³C NMR (CDCl₃) δ 30.0, 31.6, 33.2, 38.7, 63.0, 79.2, 88.4, 125.7, 125.8, 126.6, 126.7, 128.0, 128.2, 146.4, 146.9. EIMS: m/z (rel intensity) 282 (M⁺, 1), 264 (14), 223 (10), 205 (65), 183 (31), 165 (18), 105 (100), 77 (27). Anal. calcd for C₁₉H₂₂O₂: C, 80.82; H, 7.85. Found: C, 80.59; H, 8.02.

2,2-Diphenyl-5-(2,2-dimethyl-3-hydroxypropyl)tetrahydrofuran (14f). White solid. M.p. 77-78°C. ¹H NMR (300 MHz, CDCl₃) δ 1.04 (3H, s), 1.07 (3H, s), 1.29 (1H, dd, J = 12.6, 9.3 Hz), 1.52-1.64 (2H, m), 1.75 (1H, dd, J = 12.3, 6.6 Hz), 2.44 (2H, dt, J = 1.8, 7.2 Hz), 3.46 (2H, AB, J = 7.8 Hz), 3.84 (1H, s), 4.02-4.08 (1H, m), 7.16-7.46 (10H, m). ¹³C NMR (CDCl₃) δ 26.5, 26.6, 30.5, 38.9, 39.6, 46.8, 77.6, 79.8, 89.8, 126.0, 126.2, 126.5, 126.6, 128.0, 147.2, 147.7. EIMS: m/z (rel intensity) 310 (M⁺, 4), 293 (1), 233 (5), 183 (100), 105 (45), 77 (19). HRMS calcd for C₂₁H₂₆O₂: 310.1933. Found: 310.1904.

2,2-Diphenyl-5-(4-hydroxybutyl)tetrahydrofuran (14g). Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.43-1.79 (8H, m), 1.97-2.04 (1H, m), 2.47-2.54 (1H, m), 2.59-2.67 (1H, m), 3.61 (2H, t, J = 6.3 Hz), 4.05-4.12 (1H, m), 7.13-7.45 (10H, m). ¹³C NMR (CDCl₃) δ 22.4, 31.3, 32.6, 35.9, 38.8, 62.7,

78.9, 87.8, 125.7, 125.8, 126.4, 126.5, 127.9, 128.0, 146.6, 147.2. EIMS: m/z (rel intensity) 296 (M^+ , 3), 278 (22), 219 (81), 183 (47), 105 (100), 77 (21). Anal. calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.82; H, 8.11.

Typical procedure for the preparations of **25**.

Triethylborane (0.2 mL, 0.2 mmol, 1 M solution in hexane) was added to the mixture of methyl iodoacetate (0.48 g, 2.4 mmol) and allyl alcohol (0.25 mL, 3.5 mmol) in anhydrous CH_2Cl_2 (10 mL) and the resulting solution was stirred at room temperature for 1 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane / ethyl acetate (4:1, v:v) as the eluent to give the pure product methyl 5-hydroxy-4-iodopentanoate **25a** as a colorless liquid. Yield: 538 mg (87%). IR (film): ν (cm^{-1}) 3450, 1736. 1H NMR (300 MHz, $CDCl_3$) δ 2.13-2.19 (2H, m), 2.42-2.64 (2H, m), 2.70 (1H, br), 3.70 (3H, s), 3.75-3.83 (2H, m), 4.21-4.30 (1H, m). EIMS: m/z (rel intensity) 241 ($M^+ + 1 - H_2O$, 2), 131 (3), 99 (100), 71 (72), 59 (32), 43 (53). Anal. calcd for $C_6H_{11}IO_3$: C, 27.93; H, 4.30. Found: C, 28.12; H, 4.31.

5-Acetoxy-4-iodopentanoic acid (25b). Yield: 90%. Pale yellow oil. IR (film): ν (cm^{-1}) 3100, 1741, 1710. 1H NMR (300 MHz, $CDCl_3$) δ 2.00-2.24 (5H, m), 2.50-2.75 (2H, m), 4.22-4.30 (2H, m), 4.39-4.44 (1H, m), 8.76 (1H, br). EIMS: m/z (rel intensity) 254 (1), 227 (6), 159 (100), 127 (8), 117 (79), 99 (91), 71 (20). Anal. calcd for $C_7H_{11}IO_4$: C, 29.39; H, 3.88. Found: C, 29.52; H, 3.95.

Methyl 5-acetoxy-4-iodopentanoate (25c). Yield: 91%. Colorless oil. IR (film): ν (cm^{-1}) 1738. 1H NMR (300 MHz, $CDCl_3$) δ 1.97-2.23 (5H, m), 2.41-2.66 (2H, m), 3.69 (3H, s), 4.18-4.28 (2H, m), 4.36-4.46 (1H, m). EIMS: m/z (rel intensity) 227 (6), 204 (6), 173 (15), 131 (11), 108 (28), 91 (94), 71 (29), 43 (100). Anal. calcd for $C_8H_{13}IO_4$: C, 32.02; H, 4.37. Found: C, 32.19; H, 4.37.

Table S1. 1H NMR Spectrum of Compound **14d**.

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