A Flexible Route Toward Polypropylene Model Compounds of Various Tacticities
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Received: The date will be inserted once the manuscript is accepted.

1. Large scale synthesis of 2,4,8,10-tetramethyl-6-methylene-undecane (6)

(E)- and (Z)-Ethyl 3,5-dimethyl-2-hexenoate (1)
To a three-neck round-bottom flask under argon atmosphere was added sodium ethoxide (933 mL, 21 wt% in ethanol, 2.50 mol) and triethyl phosphonoacetate (500 mL, 2.50 mol) at room temperature. Five minutes later, 4-methyl-2-pentanone (313 mL, 2.50 mol) was added in one portion and an exothermic reaction occurred. After 30 minutes, the mixture was heated under reflux for 1.5 hours. The mixture was then distilled under atmospheric pressure to eliminate ethanol until the temperature of the vapor reached 90 °C. The mixture was finally cooled down to room temperature and dichloromethane (400 mL) as well as cold water (800 mL) were added. The aqueous layer was extracted with dichloromethane (2 x 400 mL) and the combined organic layers were washed with water (2 x 1000 mL) and dried over MgSO4. The crude product was distilled under vacuum.
Yield: 391.6 g (2.30 mol, 92 %), colorless oil.

\[ \delta = 5.63 \text{ (s, 1 H, E-\( \alpha,\beta \))}, 5.71 \text{ (s, 1 H, Z-\( \alpha,\beta \))}, 5.10 \text{ (d, } J^3 = 9 \text{ Hz, 1 H, E-\( \beta,\gamma \))}, 5.15 \text{ (d, } J^3 = 9 \text{ Hz, 1 H, Z-\( \beta,\gamma \))}. \]

Ethyl 3,5-dimethylhexanoate (2)
To a three-neck round-bottom flask was added the mixture of isomers of unsaturated ester (1) (91.88 g, 540 mmol) and 10% Pt/C (~ 3 g, ~ 150 μmol). The atmosphere in the flask was purged three times with argon and three times with hydrogen. The reaction mixture was stirred vigorously at 30 °C under hydrogen atmosphere (~ 1 atm) for 9 days. The catalyst was then filtered and washed with petroleum ether (3 x 300 mL). The pure product was recovered after distillation of the solvent.
Yield: 92.38 g (536 mmol, 99 %), colorless oil.

\[ \delta = 4.13 \text{ (q, } J^3 = 7 \text{ Hz, 2 H), 2.19-2.33 (m, 1 H), 1.93-2.12 (m, 2 H), 1.63 (m, 1 H), 1.26 (t, } J^3 = 7 \text{ Hz, 3 H), 1.01-1.18 (m, 2 H), 0.91 (d, } J^3 = 6 \text{ Hz, 3 H), 0.87 (2d, } J^3 = 6 \text{ Hz, 6 H)}. \]

Dimethyl 4,6-dimethyl-2-oxoheptylphosphonate (3)
A two-neck flask under argon atmosphere containing BuLi (100 mL, 2.5 M in hexanes, 250 mmol) and anhydrous THF (250 mL) was cooled down to -78 °C (dry-ice / isopropanol). Dimethyl methylphosphonate (31.1 g, 250 mmol) was then added dropwise in 5 minutes. The colorless solution turned into a white gel. The mixture was stirred at -78 °C for 30 minutes. A solution of ethyl 3,5-dimethylhexanoate (2) (15 g, 87.25 mmol) in anhydrous THF (10 mL) was then added dropwise. The mixture turned into a colorless liquid again. The temperature was then allowed to rise up to ~20 °C in 2 h. A saturated solution of NH₄Cl (100 mL) was then added to the mixture. The aqueous layer was extracted with dichloromethane (2 x 100 mL). The organic layers were washed with water (2 x 200 mL) and with brine (2 x 200 mL), dried over MgSO₄.
filtered and concentrated. The crude product (21.05 g, ~ 84 mmol, 1H NMR conversion 99%) was not purified and used as such in the following step of the synthesis.

1H NMR (300 MHz, CDCl3): δ = 3.79 (d, J³ = 11 Hz, 6 H), 2.98-3.18 (m, 2 H), 2.52-2.62 (dd, J³ = 5 Hz, J² = 17 Hz, 1 H), 2.36-2.47 (dd, J³ = 8 Hz, J² = 17 Hz, 1 H), 2.09 (m, 1 H), 1.62 (m, 1 H), 1.00-1.16 (m, 2 H), 0.84-0.90 (m, 9 H).

13C NMR (75 MHz, CDCl3): δ = 201.6, 52.9, 51.8, 46.3, 41.8, 26.7, 25.3, 23.2, 22.2, 19.8.

(E)-2,8,10-Trimethyl-4-undecene-6-one (4)

NaH (3.36 g, 84.1 mmol, 60% in mineral oil) was washed in a two-neck flask under argon atmosphere with petroleum ether (3 x 30 mL) and dried under vacuum. Anhydrous THF (100 mL) was then poured onto NaH and cooled down to 0 °C. Dimethyl 4,6-dimethyl-2-oxoheptylphosphonate (3) (21.05 g, ~ 84 mmol) was then added dropwise in 15 minutes. After 15 additional minutes isovaleraldehyde (9 mL, 84 mmol) was slowly added to the mixture. The mixture was stirred at 0 °C for 15 minutes. Water (150 mL) and Et2O (150 mL) were then added. The aqueous layer was extracted with Et2O (3 x 150 mL). The organic layers were washed with brine (2 x 250 mL), dried over MgSO4, filtered and concentrated. The crude product (17.67 g, ~ 84 mmol, 1H NMR conversion 96%) was not further purified and used as such in the following step of the synthesis.

1H NMR (300 MHz, CDCl3): δ = 6.79 (dt, J³ = 7.5 Hz, J² = 15 Hz, 1H), 6.09 (dd, J³ = 2 Hz, J² = 15 Hz, 1 H), 2.44-2.52 (dd, J² = 6 Hz, J³ = 15 Hz, 1 H) 2.27-2.36 (dd, J² = 7.5 Hz, J³ = 15 Hz, 1 H) 2.00-2.18 (m, 3 H), 1.78 (m, 1 H), 1.62 (m, 1 H), 1.01-1.8 (m, 2 H), 0.93 (d, J³ = 7 Hz, 6 H), 0.85-0.90 (m, 9 H).

13C NMR (75 MHz, CDCl3): δ = 200.7, 146.1, 131.9, 48.2, 46.9, 41.9, 28.1, 27.8, 25.5, 23.5, 22.6, 22.4, 20.2.

2,4,8,10-Tetramethylundecan-6-one (5)

CuI (1.60 g, 8.4 mmol) and anhydrous Et2O (250 mL) were inserted in a three-neck flask under argon atmosphere. The mixture was stirred at room temperature for 10 minutes. The mixture containing 2,4,8,10-tetramethylundecan-6-one (vide supra, 17.2 g, 68.5 mmol of (5)) was then added dropwise. The reaction was stopped after 2 hours of stirring at room temperature by addition of water (100 mL) and AcOEt (100 mL). The aqueous layer was then extracted with AcOEt (3 x 200 mL). The organic layers were washed with water (2 x 300 mL) and with brine (2 x 200 mL). The white solid then disappeared. The crude product (17.22 g, 76 mmol) was recovered after drying over MgSO4, filtration and evaporation of the solvent. The crude product was not further purified and used as such in the following step of the synthesis.

1H NMR (300 MHz, CDCl3): δ = 2.28-2.37 (dd, J² = 5 Hz, J³ = 15 Hz, 2 H), 1.99-2.21 (m, 4 H), 1.61 (m, 2 H), 0.98-1.14 (m, 4 H), 0.83-0.90 (m, 18 H).

13C NMR (75 MHz, CDCl3): δ = 211.3, 146.1, 131.9, 48.2, 46.9, 41.9, 28.1, 27.8, 25.5, 23.5, 22.6, 22.4, 20.2.

2,4,8,10-Tetramethyl-6-methylene-undecane (6)

Methyltriphenylphosphonium bromide (54.29 g, 152 mmol) and t-BuOK (152 ml, 1.0 M in THF, 152 mmol) were inserted into a three-neck round-bottom flask under argon atmosphere. The mixture was stirred at room temperature for 10 minutes. The mixture containing 2,4,8,10-tetramethylundecan-6-one (vide supra, 17.2 g, 68.5 mmol of (5)) was then added dropwise. The reaction was stopped after 2 hours of stirring at room temperature by addition of water (100 mL) and AcOEt (100 mL). The aqueous layer was then extracted with AcOEt (3 x 100 mL). The combined organic layers were washed with water (2 x 200 mL), then brine (2 x 200 mL), dried over MgSO4, filtered and concentrated. The crystallization of triphenylphosphine oxide occurred during evaporation of the solvent. This solid was then triturated in pentane (100 mL) and filtered. This procedure was repeated several times. The combined filtrates were concentrated and the crude product was purified by flash chromatography (silica gel, petroleum ether 100%).

Yield: 13.86 g (61.8 mmol, 71% over 4 steps), colorless liquid.
1H NMR (300 MHz, CDCl3): \( \delta = 4.71 \) (s, 2 H), 1.90-2.08 (m, 2 H), 1.58-1.80 (m, 6 H), 0.79-1.18 (m, 22 H).

13C NMR (75 MHz, CDCl3): \( \delta = 147.57, 111.94, 111.83, 47.17, 46.76, 44.48, 44.18, 28.40, 28.29, 25.43, 23.74, 23.60, 22.47, 22.30, 20.08, 19.83. \)

2. Synthesis of 2,4,8,10-tetramethyl-6-\( ^{13}C \)-methylundecane

**2,4,8,10-Tetramethyl-6-\( ^{13}C \)-methylene-undecane**

\( ^{13}C \)-methyltriphenylphosphonium iodide (0.245 g, 0.6 mmol) and t-BuOK (0.6 ml, 1.0 M in THF, 0.6 mmol) were inserted into a three neck round bottom flask under argon atmosphere. The mixture was stirred at room temperature for 7 minutes. 2,4,8,10-Tetramethylundecan-6-one (0.138 g, 0.6 mmol) was then added dropwise. The reaction was stopped after 3.5 hours of stirring at room temperature by addition of 1 mL of water and 10 mL of AcOEt. The aqueous layer was then extracted with AcOEt (3 x 5 mL). The combined organic layers were washed with water (1 mL), then with brine (3 x 1 mL), dried over MgSO4, filtered and concentrated. The crystallization of triphenylphosphine oxide occurred during evaporation of the solvent. The solid was then triturated in pentane and filtered. This procedure was repeated several times. The combined filtrates were concentrated purified by flash chromatography (silica gel, petroleum ether 100%).

Yield: 0.009 g (0.04 mmol, 7%), colorless liquid.

1H NMR (300 MHz, CDCl3): \( \delta = 4.70 \) (d, \( J_{\text{H-13C}} = 155 \) Hz, 2 H), 1.89-2.08 (m, 2 H), 1.58-1.81 (m, 6 H), 0.79-1.18 (m, 22 H).

13C NMR (75MHz, CDCl3): Other signals in baseline noise.

2.4,8,10-Tetramethyl-6-\( ^{13}C \)-methylundecane

To a three-neck round-bottom flask was added 2,4,8,10-tetramethyl-6-\( ^{13}C \)-methylene-undecane (0.009 g, 0.04 mmol) and 10% Pt/C (5 mg). The atmosphere in the flask was purged three times with argon and three times with hydrogen. The reaction mixture was stirred at 25 °C under hydrogen atmosphere (~ 1 atm) for 43 hours. The catalyst was then filtered by using hexane as solvent and the crude product was recovered after distillation of the solvent and was not further purified.

Yield: 0.010 g (0.04 mmol, 98% conversion), colorless liquid.

1H NMR (300 MHz, CDCl3), mixture of isomers: \( \delta = 1.46-1.74 \) (m, 5 H), 0.75-1.22 (m, 29 H).

13C NMR (75MHz, CDCl3), mixture of isomers: \( \delta = 48.08, 47.80, 47.13, 46.75, 46.20, 46.10, 45.01, 27.68-27.80, 27.40-27.43, 25.34-25.43, 24.00, 23.85, 23.54, 23.43, 22.72, 22.64, 22.37, 22.21, 21.01, 20.79, 20.43-20.46, 20.07, 19.85, 19.65. \)