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Tsuji–Trost allylation of CH acids in supercritical carbon dioxide: advantages and problems

Andrei A. Vasil'ev, Ilya V. Kuchurov and Sergei G. Zlotin

Experimental details

Allylation of CH acids in $scCO_2$. Catalyst $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), CH-acid **1a-e**, **4** or **5** (1 mmol), allyl acetate (0.3 ml, ~ 3 mmol), K_2CO_3 (345 mg, 2.5 mmol) and 18-crown-6 (13 mg) were placed open to air into a 10 ml autoclave (in some experiments other bases or catalysts were used in equivalent amounts; when CH-acids were **4** and **5**, amount of base was halved). The vessel was filled with $scCO_2$ by means of a syringe-press to a total pressure of 60 atm. The mixture was allowed to equilibrate to the reaction temperature (30 min) and then additional CO_2 was pumped in to adjust pressure to 75 atm. After this, the mixture was stirred for 18 h at specified temperature. The vessel was cooled and slowly depressurized. The autoclave content was treated with CH_2Cl_2, filtered through silica gel and concentrated. The residue was analyzed by GC and/or subjected to column chromatography (silica gel, gradient 0→6% EtOAc in light petroleum) to afford products **2,3,6,7,9**, whose NMR data were close to earlier reported.

Allylation of CH acids in CH_2Cl_2. A Schlenk tube equipped with a stirring magnet and charged with CH acid **1** (0.5 mmol), catalyst $Pd(PPh_3)_4$ (*ca*. 12 mg, 2 mol%), 18-crown-6 (13 mg) and CH_2Cl_2 (1 ml) was three times deaerated by careful evacuation and filling with argon. Allyl acetate **2** (0.15 ml, ~ 1.5 mmol) was added, and the mixture was stirred for 10 min, followed by freshly powdered potassium carbonate (207 mg, 1.5 mmol). Each opening of the Schenk tube was followed by evacuation and filling with argon. The mixture was stirred at ambient temperature for 18 h. A probe was treated with water, extracted with ether and analysed by gas chromatography. To isolate the products, the reaction mixture was treated with water, extracted with ether, the extracts were dried (Na_2SO_4), concentrated and the residue was subjected to column chromatography (gradient 0→6% EtOAc in light petroleum). Yields of the products thus obtained (%): **3a**, 100 (GC); **3b**, 100 (GC), 92 (isolated); **3c**, 100 (GC); **3d**, 100 (GC), 86 (isolated); **3e**, 100 (GC), 81 (isolated); **6**, 100 (GC), 94 (isolated).

Ethyl 2-acetylpent-4-enoate **2b**. ^{1}H NMR ($CDCl_3$) δ: 1.24 (t, 3H, *J* 7.1 Hz), 2.20 (s, 3H), 2.26 (br t, 2H, *J* 7.0 Hz), 3.49 (t, 1H, *J* 7.4 Hz), 4.17 (q, 2H, *J* 7.1 Hz), 5.02 (d, 1H, *J* 12.3 Hz), 5.07 (d, 1H, *J* 17.4 Hz), 5.72 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.0 (CH_3), 28.9 (CH_3), 32.1 (CH_2), 59.2 (CH), 61.3 (OCH_2), 117.3 (=CH_2), 134.2 (=CH), 169.1 (C=O), 202.2 (C=O). The spectra were similar to earlier reported.[1,2]

Ethyl 2-allyl-2-acetylpent-4-enoate **3b**. ^{1}H NMR ($CDCl_3$) δ: 1.27 (t, 3H, *J* 7.1 Hz), 2.14 (s, 3H), 2.61 (m, 4H), 4.20 (q, 2H, *J* 7.1 Hz), 5.09 (d, 2H, *J* 11.6 Hz), 5.11 (d, 2H, *J* 15.4 Hz), 5.60 (m, 2H). The spectrum was similar to earlier reported.[1]

Ethyl 2-allyl-2-cyanopent-4-enoate **3c**. ^{1}H NMR ($CDCl_3$) δ: 1.31 (t, 3H, *J* 7.1 Hz), 2.60 (m, 4H), 4.25 (q, 2H, *J* 7.1 Hz), 5.23 (2H, *J* 15.2 Hz), 5.25 (2H, *J* 11.9 Hz), 5.81 (m, 2H). The spectrum was similar to earlier reported.[1,3]

3-Allylpentane-2,4-dione **2d**, *keto and enol forms*, 1:1. ^{1}H NMR ($CDCl_3$) δ: 2.07 (s, CH_3 keto), 2.16 (s, CH_3 enol), 2.53 (t, *J* 6.9 Hz, CH_2 keto), 2.96 (br d, *J* 4.9 Hz, CH_2 enol), 3.71 (t, *J* 7.3 Hz, CH keto), 5.68 and 5.81 (both m, =CH keto and enol), 16.70 (s, OH enol). ^{13}C NMR ($CDCl_3$) δ: 22.8 and 29.2 (CH_3), 31.1 and 32.2 (CH_2), 68.0 (CH keto), 107.5 (=C enol), 114.9 and 117.5 (=CH_2), 134.1 and 135.6 (=CH), 191.4 (C=O enol), 203.6 (C=O keto). The spectra were similar to earlier reported.[2]

3,3-Diallylpentane-2,4-dione **3d**. ^{1}H NMR ($CDCl_3$) δ: 2.04 (s, 6H), 2.59 (d, 4H, *J* 7.1 Hz), 5.03 (d, 2H, *J* 8.6 Hz), 5.05 (d, 2H, *J* 18.6 Hz), 5.45 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 27.0 (CH_3), 34.9 (CH_2), 70.2 (C), 119.1 (=CH_2), 131.9 (=CH), 205.5 (C=O). The spectra were similar to earlier reported.[2]

2-Cyanopent-4-enonitrile **2e**. ^{1}H NMR ($CDCl_3$), characteristic signals δ: 2.76 (t, 2H, *J* 6.7 Hz), 3.79 (t, 1H, *J* 6.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.9 (CH), 34.6 (CH_2), 112.1 (CN), 122.3 (=CH_2), 129.1 (=CH). The spectra were similar to earlier reported.[4]

2-Allyl-2-cyanopent-4-enonitrile **3e**. ^{1}H NMR ($CDCl_3$) δ: 2.69 (d, 4H, *J* 7.2 Hz), 5.41 (d, 2H, *J* 16.8 Hz), 5.45 (d, 2H, *J* 9.6 Hz), 5.90 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 37.2 (C), 40.8 (CH_2), 114.8 (CN), 123.2 (=CH_2), 128.4 (=CH). The spectra were similar to earlier reported.[5]

Ethyl 2-cyano-2-phenylpent-4-enoate **6**. ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, 3H, *J* 7.1 Hz), 2.86 (dd, 1H, *J* 13.9 Hz, *J* 7.0 Hz), 3.12 (dd, 1H, *J* 13.9 Hz, *J* 7.3 Hz), 4.24 (m, 2H), 5.22 (d, 1H, *J* 9.9 Hz), 5.27 (d, 1H *J* 16.3 Hz), 5.75 (m, 1H), 7.32-7.45 (m, 3H), 7.56 (d, 2H, *J* 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.7 (CH_3), 42.2 (CH_2), 54.0 (C), 63.1 (OCH_2), 117.9 (CN), 121.1 (=CH_2), 126.1 (CH arom), 128.8 (CH arom), 129.0 (CH arom), 130.6 (=CH), 134.1 (C arom), 167.0 (C=O). The spectra were similar to earlier reported.[6]

Ethyl 1-allyl-2-oxocyclopentanecarboxylate **7**. ^{1}H NMR ($CDCl_3$) δ: 1.24 (t, 3H, *J* 7.1 Hz), 1.85-2.06 (m, 3H), 2.15-2.29 (m, 1H), 2.31-2.50 (m, 3H), 2.66 (dd, 1H, *J* 13.9 Hz, *J* 7.2 Hz), 4.15 (q, 2H, *J* 7.1 Hz), 5.08 (d, 1H, *J* 11.0 Hz), 5.10 (d, 1H, *J* 16.1 Hz), 5.69 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.0 (CH_3), 19.4 (CH_2), 32.1 (CH_2), 37.8 (CH_2), 38.0 (CH_2), 59.9 (C), 61.4 (CH_2), 118.9 (=CH_2), 133.0 (=CH), 170.8 (C=O), 214.4 (C=O). The spectra were similar to earlier reported.[7]

Compounds **9**, **9'**, **9''** and **9'''** in a ratio 32:18:21:29 were obtained as an inseparable by column chromatography mixture.

Ethyl 2-cyano-5-methylhex-4-enoate **9**. ^{1}H NMR ($CDCl_3$) δ: 1.31 (d, 3H, *J* = 7.3 Hz), 1.67 (br. s, 3H), 1.74 (br. s, 3H), 2.65 (t, 2H, *J* = 6.6 Hz), 3.47 (t, 1H, *J* = 6.6 Hz), 4.26 (q, 2H, *J* = 6.8 Hz), 5.18 (br. s, 1H). The spectrum was similar to earlier reported.[8,9] GC MS (*m*/*z*): M^+ 181.

Ethyl 2-cyano-3,3-dimethylpent-4-enoate **9'**. ^{1}H NMR ($CDCl_3$) δ: 1.28 (s, 6H), 1.30 (t, 3H, *J*=7.3); 3.36 (s, 1H), 4.24 (q, 2H, *J*=6.8); 5.14 (d, 1H, *J*=17.1); 5.15 (d, 1H, *J*=10.7); 5.91 (d.d, 1H, *J*=17.6, 10.8). ^{13}C NMR ($CDCl_3$) δ: 14.0 (Me); 24.5 (Me); 25.2 (Me); 40.0 (C); 48.7 (CH); 62.4 (OCH_2); 114.3 (=CH_2); 115.6 (CN); 142.2 (=CH); 164.8 (C=O). The spectra were similar to earlier reported.[8,9] GC MS (*m*/*z*): M^+ 181.

Ethyl 2-cyano-3,4-dimethylpent-4-enoate **9''**, two diastereomers. ^{1}H NMR ($CDCl_3$, characteristic signals) δ: 1.79 (br. s, 3H), 2.90 (m, 1H), 4.93 (m, 2H) was close to earlier reported[8]; other signals were overlapped with those of other isomers. GC MS (*m*/*z*): M^+ 181.

Ethyl 2-cyano-4-methylhex-4-enoate **9'''**, *E*,*Z* isomers. ^{1}H NMR ($CDCl_3$, characteristic signals) δ: 1.62 and 1.65 (both br.d, 3H, *J*=7.1), 1.77 (br.s), 5.45 (m) was close to earlier reported[8]; other signals were overlapped with those of other isomers. GC MS (*m*/*z*): M^+ 181.

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