Solvent Dependent Chemoselectivities in Ce(IV) Mediated Oxidative Coupling Reactions

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Supporting Information

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Materials and general methods

All oxidative additions were carried out in a glove dry box (Innovative Technology Inc.) containing a nitrogen atmosphere. Tetrabutyl Ammonium Cerium Nitrate (CTAN) was prepared according to the literature procedure.[1] All substrates were purchased from Aldrich and used without further purification. CH_3CN was distilled from CaO under nitrogen, and CH_2Cl_2 was distilled from CaH_2 under nitrogen. CV studies carried out on Bas 100B Electrochemical Analyzer. NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. Mass spectra were performed on a Thermoquest 2000 series trace ion trap GC-MS.

Procedure (A) for the oxidative addition reactions carried out in CH_3CN:

Ceric tetrabutyl ammonium nitrate (CTAN, 2.2mmol, in 5ml CH_3CN) solution was added to a stirred mixture of 1,3-dicarbonyl compounds (**1-6**, 1mmol) and allyltrimethyl silane (1.2mmol) in 5ml CH_3CN within 5 mins. After 4 hrs, the reaction solution was poured into cold water and extracted with 4 x 25ml ether. The organic extracts were dried over $MgSO_4$ and concentrated. The residue was chromatographed with a silica gel column.

Procedure (B) for the oxidative addition reactions carried out in CH_2Cl_2:

Ceric tetrabutyl ammonium nitrate (CTAN, 2.2mmol, in 5ml CH_2Cl_2 solution) was added to a stirred mixture of 1,3-dicarbonyl compounds (**1-6**, 1mmol) and allyltrimethyl silane(1.2mmol) in 5ml CH_2Cl_2 over a 5 min. period. After 4 hrs, the reaction solution was diluted with 50ml of CH_2Cl_2. The reaction solution was poured into cold water, and washed with cold water. The organic layer was dried over $MgSO_4$ and concentrated. A red residue was obtained after concentration as CTAN has higher solubility in the CH_2Cl_2 than water. The product was separated on a silica gel column (30X10cm)1:1 EtOAc and hexane. The product was concentrated via rotary evaporation and provided a light colored organic residue.

Procedure for the CV studies of the redox potentials of Ce(IV) compound:

The redox potentials of CTAN in CH_3CN and CH_2Cl_2 were measured by cyclic voltammetry with a BAS 100B electrochemical analyzer. The working electrode was a standard glassy carbon electrode. The auxiliary electrode was a platinum wire and a saturated $Ag/AgNO_3$ electrode was used as the reference electrode. The electrolyte was tetrabutylammonium hexafluorophosphate. All measurements were repeated twice and no significant experimental error was observed between the two measurements.

The experimental conditions were as follows:

Initial E (mV) = 1400
Final E (mV) = 0
Sweep rate (mV/s) = 100
Quiet T (s) = 2
Sensitivity = (A/V) =1 x 10-5

Preparation of 1A in CH_3CN:

The procedure (A) was followed by the use of 0.116g methylacetoacetate, 0.136g allyl trimethylsilane and 2.1g CTAN. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/10) provided 0.126g product 1A(GC tR: 6.94min, TLC R_f 0.45, EtOAc/hexane: 1/5) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 2.24 (s, 3H); 2.54-2.60 (m, 2H); 3.49-3.54(m, 1H); 3.74(s, 3H); 5.01-5.10(m, 2H); 5.67-5.79(m, 1H). ^{13}C NMR($CDCl_3$) δ 29.16; 32.20; 52.42; 59.08; 117.54; 134.11; 169.71; 202.38. Mass M^+ 156(2); 125(7);113(85);97(20);81(100); 53(76).

Preparation of 1B in CH_2Cl_2:

The procedure (B) was followed by the use of 0.116g methylacetoacetate, 0.138g allyl trimethylsilane and 2.12g CTAN. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/10) provided 0.163g product 1B(GC tr: 14.32min, TLC R_f 0.55, EtOAc/hexane: 1/5) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.044(s,9H); 0.99-1.03(dd, 1H); 1.16-1.20(dd, 1H); 2.14(s, 3H); 2.40-2.46(dd, 1H); 2.94-3.00(dd, 1H); 3.68(s, 3H), 4.68-4.78(m, 1H). ^{13}C NMR($CDCl_3$) δ -0.997; 14.27; 25.45; 37.80; 50.69; 81.65; 101.21; 166.84; 168.02. Mass M^+ 228(0.6);181(100); 166(23); 151(13); 109(15); 89(28); 73(86).

Preparation of 2A in CH_3CN:

The procedure (A) was followed by the use of 0.130g ethyl acetoacetate, 0.136g allyl trimethylsilane and 2.1g CTAN. Purification by flash chromatography(25 X 30cm, EtOAc/Hexane:1/10) provided 0.124g product 2A(GC tR: 8.42min, TLC R_f 0.40, EtOAc/hexane: 1/5) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.22 (t, 3H); 2.18 (s, 3H); 2.51-2.56(m, 2H); 3.42-3.49(m, 1H); 4.15(q, 2H); 4.98-5.07(m, 2H); 5.62-5.75(m, 1H). ^{13}C NMR($CDCl_3$) δ 13.11; 28.96; 32.02; 59.28; 61.32; 117.22; 134.11; 169.16; 202.30. Mass M^+ 170(3); 127(100);100(43);99(48);83(28); 81(42); 55(36).

Preparation of 2B in CH_2Cl_2:

The procedure (B) was followed by the use of 0.130g methyl acetoacetate, 0.136g allyl trimethylsilane and 2.14g CTAN. Crude NMR showed a mixture of 2A and 2B. GC showed that the ratio of 2A and 2B in the crude product is 1: 4.2. Purification by flash chromatography(25 X 30cm, EtOAc/Hexane:1/10) provided 0.150g product 2B (GC tR: 14.50min,TLC R_f 0.42, EtOAc/hexane: 1/20) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.06(s,9H); 1.01-1.06(dd, 1H); 1.12-1.18(dd, 1H); 1.25-1.27(t, 3H); 2.15(s, 3H); 2.40-2.49(dd, 1H); 2.90-3.00(dd, 1H); 4.01-4.17(q, 2H), 4.66-4.78(m, 1H). ^{13}C NMR($CDCl_3$) δ -0.95; 14.29; 14.49; 25.47; 37.88; 59.32; 81.55; 101.54; 166.49; 167.66. Mass M^+ 242(15); 227(66); 199(83); 181(100); 171(40); 153(32); 127(16); 81(22); 73(55).

Preparation of 3A in CH_3CN:

The procedure (A) was followed by the use of 0.112g (0.5mmol) 1,3-diphenyl-1,3-propanedione, 0.065g allyl trimethylsilane and 1.08g CTAN. Crude NMR showed a mixture of 3A and 3B. GC showed that the ratio of 3A and 3B in the crude product is 7.3:1. Purification by flash chromatography(15 X 25cm, EtOAc/Hexane:1/5) provided 0.103g product 3A(GC tR: 22.75min, TLC R_f 0.35, EtOAc/hexane: 1/3) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 2.82-2.88 (m, 2H); 4.98-5.06 (m, 2H); 5.25-5.29(m, 1H); 5.78-5.92(m, 1H); 7.40-7.48(m, 4H); 7.52-7.57(m, 2H); 7.92-7.95(m, 4H). ^{13}C NMR($CDCl_3$) δ 35.55; 56.79; 117.24; 128.58; 128.89; 133.54; 135.08; 195.50. Mass M^+ 264(0.2); 236(21);159(27);144(20); 105(100);77(66).

Preparation of 3B in CH_2Cl_2:

The procedure (B) was followed by the use of 0.112g methyl acetoacetate, 0.07g allyl trimethylsilane and 1.10g CTAN. Crude NMR showed a mixture of 3A and 3B. GC showed that the ratio of 3A and 3B in the crude product is 1:5.7. Purification by flash chromatography(15 X 25cm, EtOAc/Hexane:1/20) provided 0.115g product 3B(GC tR: 26.62min, TLC R_f 0.45, EtOAc/hexane: 1/10) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.129(s,9H); 1.19-1.24(dd, 1H); 1.38-1.44(dd, 1H); 2.93-2.98(dd, 1H); 3.33-3.38(dd, 1H); 4.97-5.03(m, 1H); 7.02-7.07(m, 4H); 7.13-7.22(m, 4H); 7.42-7.44(m,2H). ^{13}C NMR($CDCl_3$) δ -0.90; 25.08; 41.04; 82.03; 112.28; 127.53; 127.54; 128.88; 129.35; 129.81; 130.39; 130.90; 139.28; 166.14; 193.63. Mass M^+ 336(30); 245(52); 105(100); 77(25); 73(35).

Preparation of 4B in CH_3CN:

The procedure (A) was followed by the use of 0.112g methyl acetoacetate, 0.130g allyl trimethylsilane and 2.20g CTAN. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/4) provided 0.161g product 4B(GC tR: 17.49min, TLC R_f 0.24, EtOAc/hexane: 1/1) as a colorless liquid. ^1H NMR ($CDCl_3$) δ 0.067(s,9H); 1.02-1.10(dd, 1H); 1.20-1.27(dd, 1H); 1.96-2.04(m, 2H); 2.29-2.41(m, 5H); 2.89-2.96(m, 1H); 4.85-4.96(m, 1H). ^{13}C NMR($CDCl_3$) δ -0.98; 21.68; 24.10; 25.67; 33.97; 36.48; 85.32; 113.07; 177.22; 195.57. Mass M^+ 224(25); 209(100); 195(21); 181(52); 153(16); 133(13); 105(8); 73(91).

Preparation of 4B in CH_2Cl_2:

The procedure (B) was followed by the use of 0.112g ethyl acetoacetate, 0.130g allyl trimethylsilane and 2.21g CTAN. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/4) provided 0.174g product 4B(TLC R_f 0.24, EtOAc/hexane: 1/1) as a colorless liquid: ^1H NMR, ^{13}C NMR and GC-Mass data was the same as the shown in the last procedure.

Preparation of 5A in CH_3CN:

The procedure (A) was followed by the use of 0.1g 1,3-pentadione, 0.128g allyl trimethylsilane and 2.24g CTAN. Crude NMR showed a mixture of 5A and 5B. GC showed that the ratio of 5A and 5B in the crude product is 3.2:1. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/20) provided 0.086g product 5A(GC tR: 7.38min, TLC R_f 0.45, EtOAc/hexane: 1/10) as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 2.23(s, 6H); 2.54-2.63(m, 2H); 3.68-3.73(t, 1H); 5.06-5.12(m, 2H), 5.72-5.86(m, 1H). ^{13}C NMR($CDCl_3$) δ 22.7; 24.8; 66.8; 115.0; 136.8; 205.1. Mass M^+ 140(3); 125(8); 97(100); 79(30); 55(21).

Preparation of 5B in CH_2Cl_2:

The procedure (B) was followed by the use of 0.0996g 1,3-pentadione, 0.130g allyl trimethylsilane and 2.2g CTAN. Crude NMR showed a mixture of 5A and 5B. GC showed that the ratio of 5A and 5B in the crude product is 1: 4.5. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/10) provided 0.139g product 5B(GC tR: 12.50min, TLC R_f 0.4, EtOAc/hexane: 1/5) as a colorless liquid and 0.025g product 5A as by-product. ^{1}H NMR ($CDCl_3$) δ 0.07(s,9H); 0.95-1.02(dd, 1H); 1.13-1.20(dd, 1H); 2.10-2.14(s, 6H); 2.48-2.53(dd, 1H); 2.97-3.01(dd, 1H); 4.66-4.77(m, 1H). ^{13}C NMR ($CDCl_3$) δ -0.71; 15.47; 25.75; 29.58; 38.91; 81.93; 112.41; 167.87; 194.81. Mass M^+ 212(25); 197(60); 181(17);169(10);107(8); 73(100); 43(80).

Preparation of 6B in CH_3CN:

The procedure (A) was followed by the use of 0.170g 4-trimethylsilyloxy-3-penten-2-one, 0.128g allyl trimethylsilane and 2.1g CTAN. Purification by flash chromatography(25 X 30cm, EtOAc/Hexane:1/10) provided 0.169g product 6B(TLC R_f 0.4, EtOAc/hexane: 1/5) as a colorless liquid: ^{1}H NMR , ^{13}C NMR and GC-Mass data are the same as shown in the last procedure.

Preparation of 6B in CH_2Cl_2:

The procedure (B) was followed by the use of 0.176g 4-trimethylsilyloxy-3-penten-2-one, 0.130g allyl trimethylsilane and 2.2g CTAN. Purification by flash chromatography (25 X 30cm, EtOAc/Hexane:1/10) provided 0.157g product 6B(TLC R_f 0.4, EtOAc/hexane: 1/5) as a colorless liquid: ^{1}H NMR , ^{13}C NMR and GC-Mass data are the same as shown in the last procedure.

Reference:

1. Muathen, H.A. Ind.J.Chem.**1991**, *30B*, 522.