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

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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. CH₃CN was distilled from CaO under nitrogen, and CH₂Cl₂ was distilled from CaH₂ 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 CH₃CN:

Ceric tetrabutyl ammonium nitrate (CTAN, 2.2mmol, in 5ml CH₃CN) solution was added to a stirred mixture of 1,3-dicarbonyl compounds (**1-6**, 1mmol) and allyltrimethyl silane (1.2mmol) in 5ml CH₃CN 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 MgSO₄ and concentrated. The residue was chromatographed with a silica gel column.

Procedure (B) for the oxidative addition reactions carried out in CH₂Cl₂:

Ceric tetrabutyl ammonium nitrate (CTAN, 2.2mmol, in 5ml CH₂Cl₂ solution) was added to a stirred mixture of 1,3-dicarbonyl compounds (**1-6**, 1mmol) and allyltrimethyl silane(1.2mmol) in 5ml CH₂Cl₂ over a 5 min. period. After 4 hrs, the reaction solution was diluted with 50ml of CH₂Cl₂. The reaction solution was poured into cold water, and washed with cold water. The organic layer was dried over MgSO₄ and concentrated. A red residue was obtained after concentration as CTAN has higher solubility in the CH₂Cl₂ 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 CH₃CN and CH₂Cl₂ 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/AgNO₃ 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 CH₃CN:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) 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 CH₂Cl₂:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) -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 CH₃CN:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) 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 CH₂Cl₂:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) -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 CH₃CN:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) 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 CH₂Cl₂:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) -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 CH₃CN:

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 (CDCl₃) 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). ¹³C NMR(CDCl₃) -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 CH₂Cl₂:

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, ¹³C NMR and GC-Mass data was the same as the shown in the last procedure.

Preparation of 5A in CH₃CN:

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. ^1H NMR (CDCl_3) 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) 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. ^1H NMR (CDCl_3) 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) -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: ^1H 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: ^1H 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.