SUPPORTING INFORMATION

Copper Catalyzed Atom Transfer Radical Cascade Reactions in the Presence of Free-Radical Initiators as Reducing Agents

Carolynne Ricardo and Tomislav Pintauer*

Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, 308 Mellon Hall, Pittsburgh, PA 15282, Tel: 412-396-1626, Fax: 412-396-5683, Email: pintauert@duq.edu

Experimental Section

General Procedures. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from cold methanol and dried at room temperature under vacuum prior to use. Tris(2-pyridylmethyl)amine (TPMA)[1] and [Cu^{II}(TPMA)Cl][Cl][2] were synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on the Bruker Avance Spectrometer operating at 400 MHz and 100 MHz, respectively. Chemical shifts are given in ppm relative to residual $CDCl_3$ peak (δ7.26 ppm for ^{1}H and δ77 ppm for ^{13}C). IR spectra were recorded in the solid state or solution using Nicolet Smart Orbit 380 FT-IR spectrometer (Thermo Electron Corporation).

Catalyst Solutions. 0.01M and 0.005M solutions of [Cu^{II}(TPMA)Cl][Cl] were prepared by dissolving the copper(II) complex in MeOH using volumetric flasks to accommodate various catalyst loadings.

General Procedure for Addition of Carbon Tetrachloride to 1,6-Heptadiene Catalyzed by [Cu^{II}(TPMA)Cl][Cl] in the Presence of AIBN. All reactions were performed in disposable 5.0mm NMR tubes equipped with a plastic cap. In a typical experiment, 1,6-heptadiene (2.0 mmol, 269 μL), CCl_4 (2.5 mmol, 241μL), AIBN (0.1 mmol, 0.0164 g) and internal standard (1,4-dimethoxybenzene or toluene, 10 mol% relative to 1,6-diene) were dissolved in 510 μL of methanol in order to make the final solution 2.0M in 1,6-heptadiene. 200 μL of the stock solution (0.4 mmol 1,6-heptadiene, 0.5 mmol CCl_4 and 0.02 mmol AIBN) were then added to the NMR tube, followed by the desired amount of the copper(II) complex (from 0.01M [Cu^{II}(TPMA)Cl][Cl] and for [1,6-heptadiene]$_0$:[Cu^{II}]$_0$ ratios of 1000:1 (V= 40μL) and 2000:1 (V= 20μL), from 0.05M

[Cu^{II}(TPMA)Cl][Cl] and for [1,6-heptadiene]$_0$:[Cu^{II}]$_0$ ratio of 5000:1 (V= 16μL) and 10000:1 (V= 8μL)) and the total volume adjusted by adding methanol in order to maintain the concentration of 1,6-heptadiene at 1.0M. The NMR tube was then flushed with argon for 30 seconds, sealed with a plastic cap and teflon tape, followed by electrical tape and heated in an oil bath thermostated at 60 °C for 24h. The conversion of 1,6-heptadiene and the percent yield of the products were obtained using ^{1}H NMR spectroscopy. The *trans*- and *cis*- ratios were determined by ^{1}H NMR after solvent evaporation.

General Procedure for Addition of Carbon Tetrachloride to 1,6-Heptadiene Catalyzed by [Cu^{II}(TPMA)Cl][Cl] and V-70. Similar procedure to the one above was followed but using V-70 as the radical initiator (0.0308g, 0.1 mmol). 150 μL of the stock solution (0.3 mmol diene, 0.375 mmol CCl_4 and 0.015 mmol V-70) was then added to the NMR tube, followed by the desired amount of the copper(II) complex (from 0.01M [Cu^{II}(TPMA)Cl][Cl] and for [1,6-heptadiene]$_0$:[Cu^{II}]$_0$ ratio of 1000:1 (V= 30μL), from 0.05M [Cu^{II}(TPMA)Cl][Cl] and for [1,6-heptadiene]$_0$:[Cu^{II}]$_0$ ratio of 5000:1 (V= 12μL) and 10000:1 (V= 6μL)). The total volume was then adjusted by adding methanol maintaining the concentration of 1,6-heptadiene at 1.0M. The reaction mixture was left at room temperature (22±2 °C) or immersed in an oil bath thermostated at 30°C for a period of 24 h. The conversion of 1,6-heptadiene and the percent yield of the products were obtained using ^{1}H NMR spectroscopy. The *trans*- and *cis*- ratios were determined by ^{1}H NMR after solvent evaporation.

General Procedure for Addition of Carbon Tetrachloride to 1,6-Dienes Catalyzed by [Cu^{II}(TPMA)Cl][Cl] and AIBN/V-70. Same procedures described above were followed except that the following volumes of 1,6-diene in the stock solution were used: V(diallyl ether)=244μL, V(diethyldiallylmalonate)= 484μL, V(*tert*-butyl-*N,N*-diallylcarbamate)= 216μL) and V(*N,N*-diallyl-2,2,2-trifluoroacetamide)= 342μL). After adding CCl_4 (2.5 mmol, 241μL), reducing agent (0.1 mmol, AIBN = 0.0164 g or V-70= 0.0308 g) and internal standard (1,4-dimethoxybenzene or toluene, 10 mol% relative to 1,6-diene), methanol was added to maintain the concentration of 1,6-diene at 2.0 M (for diallyl ether = 515μL, diethyldiallylmalonate=275 μL, *tert*-butyl-*N,N*-diallylcarbamate=543μL) and *N,N*-diallyl-2,2,2-trifluoroacetamide= 417μL).

Product Characterization. ^{1}H and ^{13}C NMR spectra for all 5-*exo*-*trig* cyclic products have been reported elsewhere,[3] except for 1-(3-(chloromethyl)-4-(2,2,2-trichloroethyl)pyrrolidin-1-yl)-2,2,2-trifluoroethanone.

1-(3-(Chloromethyl)-4-(2,2,2-trichloroethyl)pyrrolidin-1-yl)-2,2,2-trifluoroethanone. ^{1}H ($CDCl_3$, 400 MHz, RT): mixture of cis and trans, δ3.95-4.10 (m, 1H), δ3.65-3.90 (m, 3H), δ3.40-3.55 (m, 2H), δ3.00-3.10 (m, 2H), δ2.80-2.85 (m, 2H).

^{13}C ($CDCl_3$, 100 MHz, RT): mixture of *cis* and *trans*, δ156.0, 155.5, 117.6, 114.7, 97.9, 53.2, 52.8, 51.1, 50.3, 49.3, 42.7, 42.0, 41.2, 39.0, 37.2.

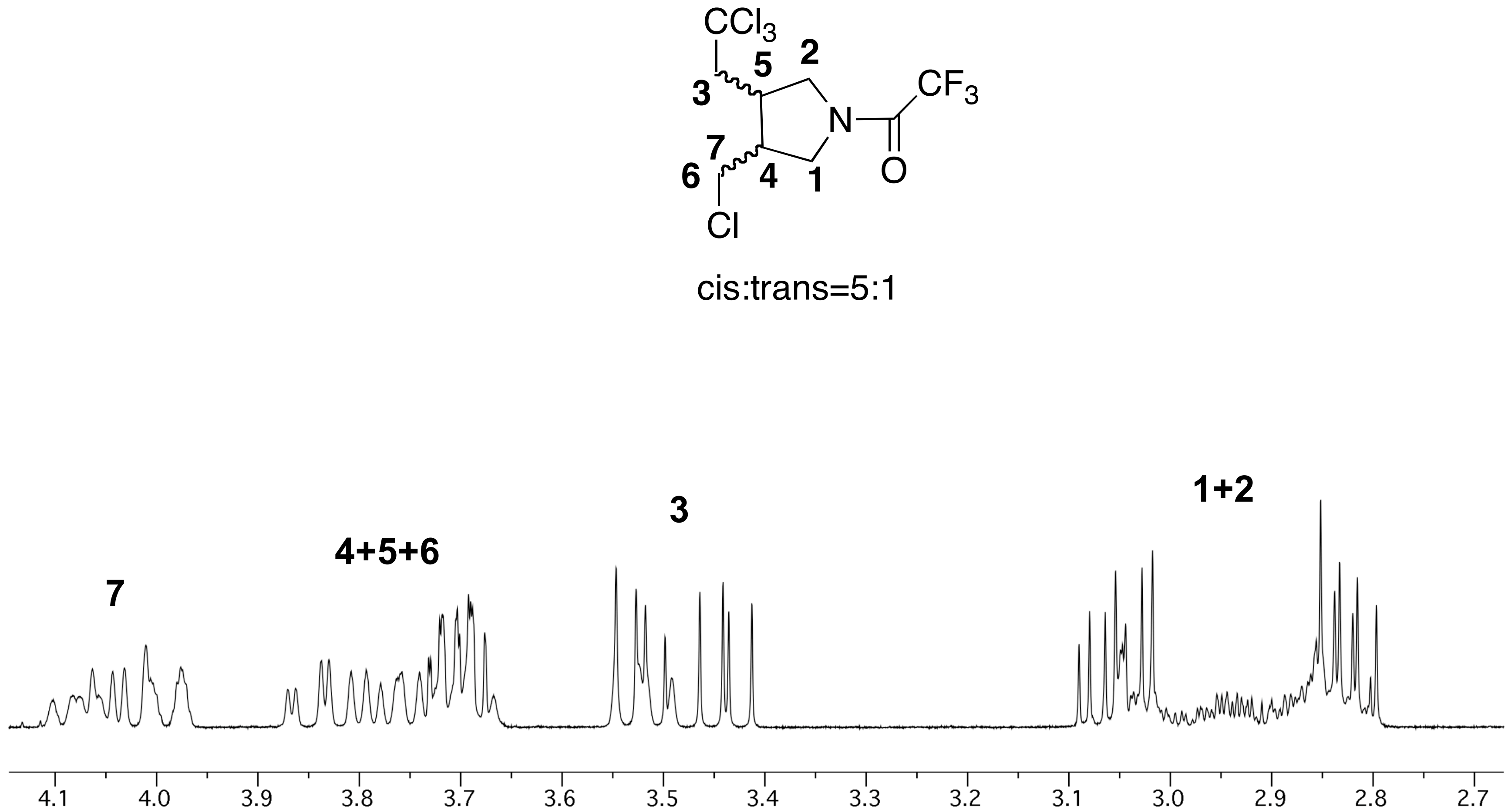

Figure 1S. ^{1}H NMR (CD_3Cl, RT, 400 MHz) spectrum of a mixture of *cis* and *trans* 1-(3-(Chloromethyl)-4-(2,2,2-trichloroethyl)pyrrolidin-1-yl)-2,2,2-trifluoroethanone.

References

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