

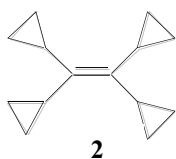
Supporting Materials

Reaction of TCPE+MTAD

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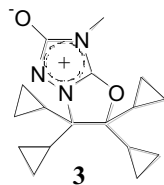
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Experimental Section: ^1H and ^{13}C NMR spectra were taken at 400 MHz and 100 MHz respectively with CD_2Cl_2 as the solvent at low temperatures and CDCl_3 at room and elevated temperature. Chemical shifts are reported in parts per million using the solvent resonance for calibration. Data are reported as follows: chemical shift, multiplicity (app = apparent, par obsc = partially obscured, ovrrp = overlapping, s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), and integration. APCI mass spectra were obtained by direct injection on a Finigan Navigator LC-PDA-MS in the Florida International University Advanced Mass Spectrometry Facility Center. Dicyclopentyl ketone, titanium (IV) chloride, zinc dust, THF, 4-methyl-1,2,4-triazoline-3,5-dione (MTAD), chloroform- d , dichloromethane- d_2 were purchased from Aldrich and used without any purification.



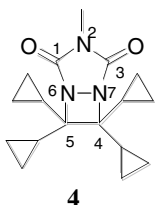
1,1,2,2-tetracyclopentylethylene (TCPE, 2): It was synthesized by McMurry reaction^{1,2}. TiCl_4 (5.3 mL, 50 mmol) was added to 130 mL of dried THF in 500 mL of round bottom flask. This reaction vessel was placed in ice water bath and 6.4 g of Zn dust (100 mmol) was added portion wise to the solution under N_2 atmosphere with stirring. The color of the solution turned from yellow to dark brown and gray slurry was formed. The slurry was allowed to stir for 15 minutes. Dicyclopentyl ketone (5.0 mL, 50 mmol) was added to 120 mL of dried

THF which was added drop wise to the TiCl_4/Zn solution over 45 minutes. Once the addition was complete, the solution was refluxed for 24 hours. The resultant reaction mixture was allowed to cool to room temperature then 20 mL of 10 % Na_2CO_3 was added. The solution was extracted three times successively with 20 mL of pentane. The pentane extracts were washed with water and saturated NaCl solution. The pentane extract was dried over anhydrous MgSO_4 . The solution was filtered and solvent was evaporated under vacuum. The crude mixture was purified by silica flash chromatography (230-400 mesh) with pentane as a solvent. The solvent was carefully evaporated and the resulting residue was further purified by vacuum distillation (70-72 $^\circ\text{C}/0.5$ torr) in a relatively low yield (~20%) of highly pure product (95%): ^1H NMR (CDCl_3): δ 1.42-1.35 (m, 4H), 0.63-0.56 (m, 8H), 0.56-0.48 (m, 8H); ^{13}C NMR (CDCl_3): δ 137.8, 13.8, 5.9.



5,5,6,6-tetracyclopentyl-3-methyl-5,6-dihydro-oxazolo[3,2-b][1,2,4]-triazolium-2-olate (3): A solution of TCPE (5 μL , 0.027 mol) in 0.75 mL of CDCl_3 in NMR tube was prepared and 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) (0.0040 g, 0.036 mmol) was added to the solution and agitated at room temperature. The red color of the MTAD quickly faded to pink with the formation of intermediate product (3) which is quite stable in refrigerator for several days:

^1H NMR (CDCl_3): δ 3.18 (s, 3H), 1.40-1.33 (m, 2H), 1.22-1.15 (m, 2H), 1.05-0.99 (m, 2H), 0.74-0.68 (m, 2H), 0.66-0.54 (m, 10H), 0.43-0.37 (m, 2H); ^{13}C NMR (CDCl_3): δ 159.2, 150.9, 107.3, 73.3, 26.4, 14.9, 13.9, 2.8, 2.4, 2.3, 2.2.



6,6,7,7-tetracyclopentyl-3-methyl-1,3,5-triaza-bicyclo[3,2,0]heptane-2,4-dione (4): The reaction of TCPE+MTAD in CDCl_3 yields intermediate product (3) which was heated to 55 $^\circ\text{C}$ in an NMR tube using a thermostated water bath. After 63 hours of heating the intermediate product (3) disappeared with simultaneous formation of the corresponding diazetaine as the major product: ^1H NMR (CDCl_3) δ 3.03 (s, 3H), 1.05-0.98 (m, 4H), 0.91-0.84 (m, 4H), 0.70-0.57 (m, 8H), 0.55-0.43 (m, 4H); ^{13}C NMR (CDCl_3) δ 160.7, 80.0, 25.8, 14.9, 3.9, 2.5.

Determination of Arrhenius plot: TCPE+MTAD \rightarrow intermediate (3): NMR tube with 0.027 mmol TCPE in 0.5 mL of CD_2Cl_2 was cooled in dry ice/acetone bath. After adding 0.036 mmol of cold MTAD dissolved in CD_2Cl_2 , NMR tube was transferred to NMR probe which had been precooled to a given temperature. Proton NMR spectra were collected with short acquisition times over the range of temperature $-50 \sim -20$ °C. Two sets of peaks were monitored and integrated (eq. 1, Figure S1) to determine rate constant from the plot of left term of eq. 1 as a function of time. A different solution was prepared and used for each temperature in determining the 2nd order rate constant ($aA + bB \rightarrow \text{product}$, $a = b$, $C_{A,0} \neq C_{B,0}$).³

$$\frac{1}{C_{MTAD,0} - C_{TCPE,0}} \ln \left(\frac{C_{TCPE,0}}{C_{MTAD,0}} \frac{C_{TCPE}}{C_{MTAD}} \right) = k_{obs} t \quad (1)$$

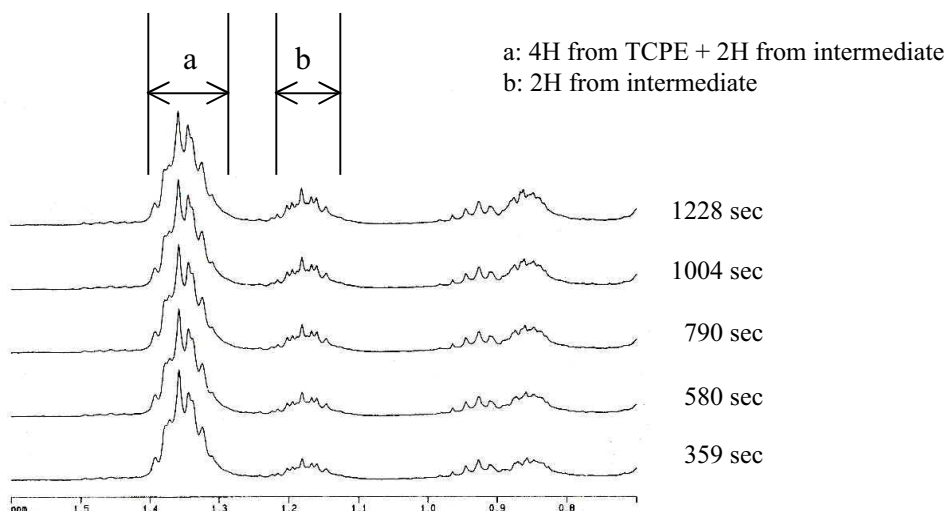


Figure S1. Proton NMR peaks from TCPE+MTAD at -30 °C.

Peak group “a” includes four protons (C-H) of TCPE and two protons (C-H) of intermediate and peak group “b” includes only two protons (C-H) of intermediate. Relative integration of peak group “b” was achieved based on the area of peak group “a”. Based on the equation, $1 - \{2 * \text{Area}(b) / (\text{area}(a) + \text{Area}(b))\} \propto$ remaining concentration of starting material (C), a plot of left term of eq. 1 as a function of time was obtained. A representative graph as a function of time (sec) at -30 °C is plotted as Figure S2. Analogous plots were obtained at -20 , -40 and -50 °C.

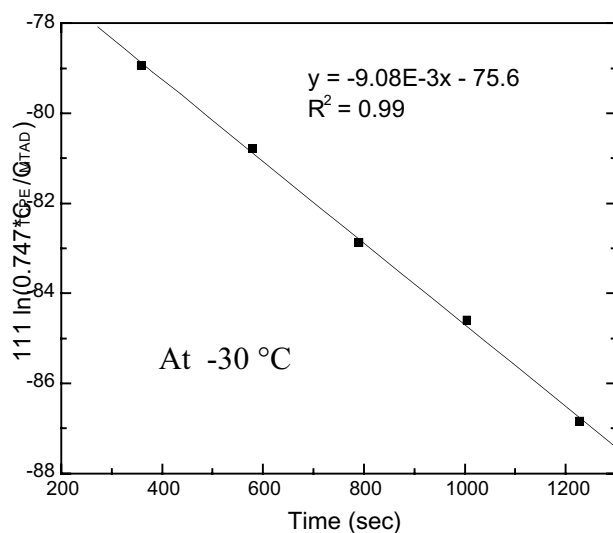


Figure S2. Plot of $1/(C_{MTAD,0} - C_{TCPE,0}) \ln(C_{TCPE,0}/C_{MTAD,0} \bullet C_{TCPE}/C_{MTAD})$ as a function of time (sec) at $-30\text{ }^{\circ}\text{C}$.

A slope (k_{obs}) of $9.08 \times 10^{-3} \text{ (mol}^{-1} \text{ sec}^{-1}\text{)}$ was obtained from the graph at -30°C . Second order rate constants were obtained at -20 , -40 and $-50\text{ }^{\circ}\text{C}$ in the same fashion yielding 2.08×10^{-2} , 5.09×10^{-3} and $2.00 \times 10^{-3} \text{ (mol}^{-1} \text{ sec}^{-1}\text{)}$, respectively.

The activation energy was obtained from the slope of the plot (Figure S3) of the logarithm of k_{obs} versus the reciprocal of the reaction temperature according to eq. 2.

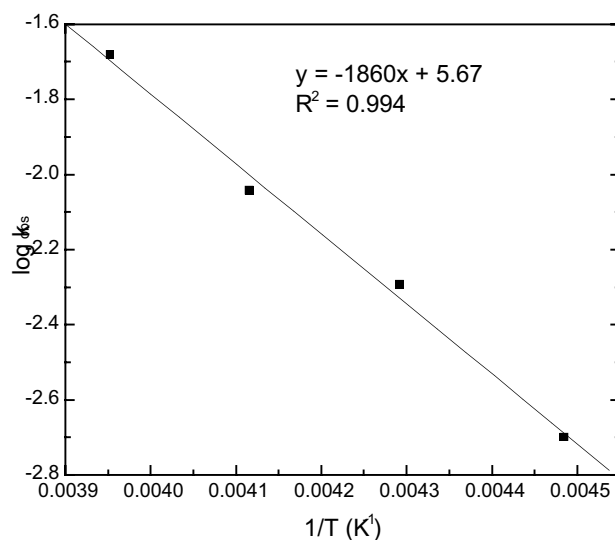


Figure S3. Arrhenius plot of log k versus 1/T for the formation of intermediate product (3).

$$\log k = \left(\frac{-E_a}{2.30R} \cdot \frac{1}{T} \right) + \log A \quad (2)$$

The slope of the graph corresponds to $-E_a/2.30R$ where E_a is activation energy (kcal mol^{-1}) for the formation of intermediate and R is gas constant ($1.98 \text{ kcal mol}^{-1} \text{ K}^{-1}$) as in eq. 2. An activation energy of $8.47 \text{ kcal mol}^{-1}$ and a pre-exponential factor of $4.68 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ were obtained at our experimental conditions.

Intermediate → diazetaine (4): NMR tube with 0.027 mmol intermediate (3) in CDCl_3 was cooled to 0°C in ice water. The NMR tube was put into preheated NMR probe with a temperatures at 40, 45, 50 and 55°C . Two sets of peaks were monitored and integrated to determine the $\ln C$ plot of intermediate product 3 as a function of time (eq. 3) to fit 1st order rate equation. Different solution was prepared for each different temperature range to fit the 2nd order rate equation. ^1H peak group of diazetaine at δ 0.91-0.84 ppm (2H from intermediate, a) was integrated and compared with peak group of intermediate at δ 1.40-1.33 ppm (4H from diazetaine, b). Based on the equation, $1 - \{\text{Area(b)}/(2 \cdot \text{area(a)} + \text{Area(b)})\}$, ∞ remained concentration of starting material (C), $\ln C$ plot of intermediate as a function of time was obtained. Different solution was prepared for each different temperature range.

$$\ln C = \ln C_0 - k_{\text{obs}} t \quad (3)$$

First order rate constants were obtained at 40, 45, 50 and 55°C yielding 3.63×10^{-6} , 6.52×10^{-6} , 9.78×10^{-6} and $1.60 \times 10^{-5} \text{ (sec}^{-1}\text{)}$, respectively. The activation energy was obtained from the slope of the plot (Figure S4) of the logarithm of k_{obs} versus the reciprocal of the reaction temperature according to eq. 2.

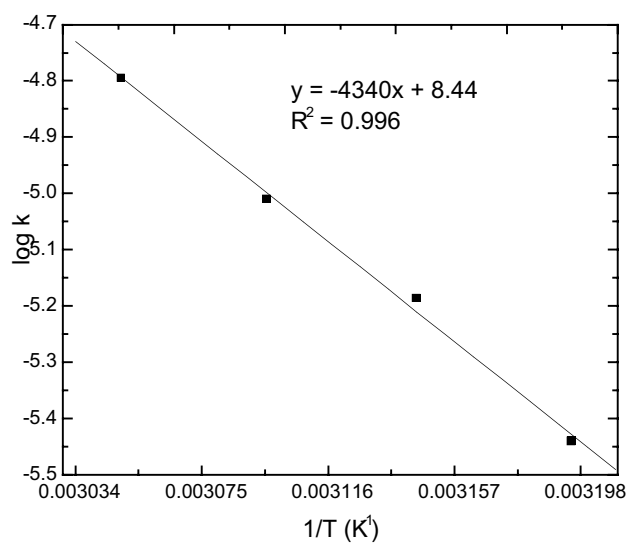


Figure S4. Arrhenius plot of $\log k$ versus $1/T$ for the formation of diazetaine product (**4**).

The activation energy of $19.8 \text{ kcal mol}^{-1}$ and a pre-exponential factor of $2.75 \times 10^8 \text{ sec}^{-1}$ were obtained from our experimental conditions.

References & Notes

1. Lenoir, D. *Synthesis* **1989**, 883-897.
2. Lenoir, D. *Synthesis* **1977**, 553-554.
3. Metz, C. R. *Schaum's Outline Series, Theory and Problems of Physical Chemistry* 2nd Ed., **1989**, McGraw-Hill Book Co. Singapore, 236-239.