Supporting Information
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Supporting Information for

The Halogenation of Aliphatic C-H Bonds with Peracetic Acid and Halide Salts

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Sample reactivity assays

Cyclohexane → Chlorocyclohexane

*Optimum Result- MeCN*

Cyclohexane (0.200 g, 2.38 mmol) and TEACl (0.395 g, 2.38 mmol) were put under N$_2$ and dissolved in 1.66 mL of MeCN. The PA (0.050 mL, 0.018 g, 0.238 mmol) was then added dropwise. After the reaction mixture was stirred for 8h at 22 °C, chlorobenzene was added as an internal standard and analyzed by GC/FID. Chlorocyclohexane is the major product with a yield of 72% compared to PA consumed. Trace amounts of cyclohexanone (1%) and polychlorinated products (<1%) were also detected. These results correspond to entry 5 on Table 1.

*Optimum Result- H$_2$O*

Cyclohexane (1.118 g, 13.2 mmol) and NaCl (3.50 g, 60 mmol) were put under N$_2$ and dissolved in 10 mL of distilled water. To this solution, PA (0.28 mL, 0.101 g, 1.32 mmol) was added in dropwise. The reaction was allowed to stir at 22 °C for 8 h. Three 5 mL portions of pentane were used to extract the product from the largely aqueous solution. The collected organic layers were combined, chlorobenzene was added as an internal standard, and the mixture was analyzed by GC. Chlorocyclohexane is produced in 59% yield. Trace amounts of cyclohexanone (1.7%) and polychlorinated cyclohexanes (5% total) were also found. These results correspond to entry 8 on Table 1.

*Isolated Yield*

In order to obtain the isolated yield, the aqueous reaction was increased in scale. Cyclohexane (33.6 g, 0.40 mol), NaCl (105 g, 1.80 mol), and 300 mL of distilled water were mixed in a 500 mL flask and degassed through N$_2$ bubbling. PA (8.4 mL, 3.02 g,
0.040 mol) was added dropwise. After the reaction was stirred at 22 °C for 8 h, four 100 mL portions of pentane were used to extract the organic products. The combined pentane extracts were washed with saturated Na₂CO₃ then distilled water. After the organic layer was dried over MgSO₄, the pentane and cyclohexane were removed under reduced pressure to yield chlorocyclohexane as a colorless liquid (1.33 g, 28% yield based on PAA consumed). ¹H NMR (400 MHz, CDCl₃, Figure S1): δ 4.01 (septet, 1H), 2.07 (m, 2H), 1.81 (m, 2H), 1.67 (m, 2H), 1.54 (m, 1H), 1.34 (m, 3H). ¹³C NMR (100 mHz, CDCl₃, Figure S2): δ 60.53, 36.89, 25.32, 25.09. HR-MS (MALDI-TOF): Calcd M, 118.0549; found, 118.0573.

Cyclohexane → Bromocyclohexane

Optimum Result- MeCN

Cyclohexane (0.200 g, 2.38 mmol) and TEABr (0.250 g, 1.19 mmol) were combined in a vial, put under N₂, and dissolved in 1.66 mL of MeCN. PA (0.10 mL, 0.036 g, 0.473 mmol) was added dropwise, and the resultant mixture was stirred at 22 °C for 8 h. Chlorobenzene was added as internal standard immediately prior to analysis by GC. Bromocyclohexane is the major product (30% yield, based on the amount of PA) with a trace amount of cyclohexanone (1%). These results correspond to entry 6 on Table 1.

Optimum Result- H₂O

Cyclohexane (1.118 g, 13.2 mmol) and NaBr (7.00 g, 68 mmol) were put under N₂ and dissolved in 10 mL of distilled water. PA (0.28 mL, 0.101 g, 1.32 mmol) was added dropwise to the resultant solution, which was allowed to stir at 22 °C for 8 h. The organic products were extracted by three 5 mL portions of pentane. Chlorobenzene was added to
the combined fractions immediately prior to analysis by GC. Bromocyclohexane is the only observed product, forming in 16% yield. These results correspond to entry 9 on Table 1.

Cyclohexene → 1,2-Dichlorocyclohexene

PA (0.42 mL, 0.15 g, 2.0 mmol) was slowly added to a solution of TEACl (0.83 g, 5.00 mmol) in 10mL of MeCN. After stirring for 5 min, 0.041g of cyclohexene (0.50 mmol) was added. The reaction mixture was analyzed by GC after stirring for 2 h at 22 °C, using chlorobenzene as an internal standard. The product was formed in 21% yield, alongside trace amounts of numerous side-products, including 3-chlorocyclohexene, and was identified by GC/MS. These results are on Table 2.

Cyclohexene → 1,2-Dibromocyclohexene

PA (0.42 mL, 0.15 g, 2.0 mmol) was slowly added to a solution of TEABr (1.05 g, 5.00 mmol) in 10 mL of MeCN. After stirring for 5 min, 0.041g of cyclohexene (0.50 mmol) was added. The reaction mixture was analyzed by GC after stirring for 2 h at 22 °C, using chlorobenzene as an internal standard. The product was formed in 77% yield and was identified by GC/MS. A single side-product, 3-bromo cyclohexene, was present in 23% yield. These results are reported on Table 2.

Adamantane → 1-Chloroadamantane

Isolated Yield

Adamantane (0.68 g, 5.00 mmol) and TEACl (8.3 g, 50 mmol) were put under N₂ and dissolved in 100 mL of CH₂Cl₂. PA (4.2 mL, 1.5 g, 20 mmol) was added dropwise to the
reaction mixture. After stirring at 22 °C for 8 h, the CH$_2$Cl$_2$ was removed under reduced pressure. The residue was neutralized with a saturated solution of Na$_2$CO$_3$ in water. The organic products were extracted from the aqueous layer with three 50 mL portions of CH$_2$Cl$_2$, which were collected, combined, and dried over MgSO$_4$. After filtration to remove the solids, the CH$_2$Cl$_2$ was evaporated, yielding a mixture of 1-chloroadamantane and 2-chloroadamantane in a 79:21 ratio. The components were separated by column chromatography (silica gel, hexane). The 1-chloroadamantane was recrystallized from hexane to yield 0.167 g (20%) of the product as a white crystalline solid. $^1$H NMR (400 MHz, CDCl$_3$, Figure S3): $\delta$ 2.14 (s, 9H), 1.68 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, Figure S4): $\delta$ 69.13, 47.94, 35.78, 31.91. HR-MS (MALDI-TOF): Calcd M, 170.0862; found, 170.0861.

**Anthracene $\rightarrow$ 9,10-Dichloroanthracene**

Anthracene (0.090 g, 0.50 mmol) and TEACl (0.83 g, 5.0 mmol) TEACl were put under N$_2$ and dissolved in 10 mL of MeCN. PA (0.42 mL, 0.15 g, 2.0 mmol) was added slowly to the reaction vessel, and the resultant mixture was allowed to stir at 22 °C for 8 h. At the end of this duration, the MeCN was removed under reduced pressure. The products were extracted from the residue with four 10 mL portions of diethyl ether. Removal of the diethyl ether yielded 9,10-dichloroanthracene (77%) as the major product, with anthroquinone (19%) and 9,10-tetrachloro-9,10-dihydroanthracene (4%) as minor products. The ratios and identities of the products were confirmed by $^1$H NMR and GC/MS. These results are summarized on Table 2.
Figure S1. $^1$H NMR of chlorocyclohexane isolated from reaction on page S4.
Figure S2. $^{13}$C NMR of chlorocyclohexane isolated from reaction on page S4.
Figure S3. $^1$H NMR of 1-chloroadamantane isolated from reaction on page S6.
Figure S4. $^{13}$C NMR of 1-chloroadamantane isolated from reaction on page S6.