

Supplementary Material

CO₂-activated NaClO-5H₂O enabled smooth oxygen transfer to iodoarene: a highly practical synthesis of iodosylarene

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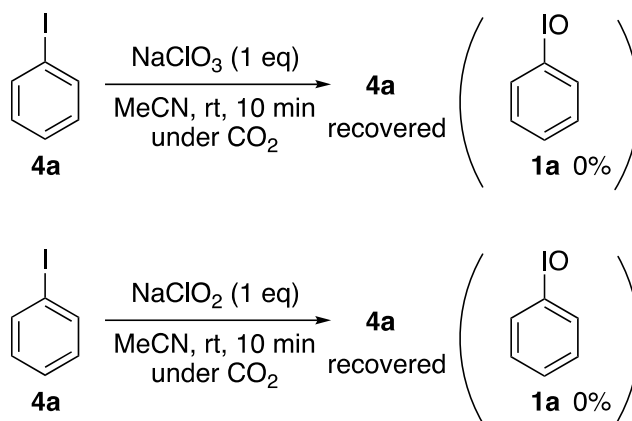
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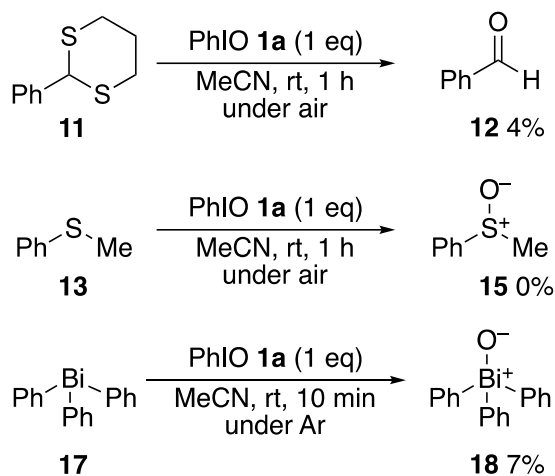
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Control experiments

**Scheme S1.** Attempted synthesis of **1a** with sodium chlorate and sodium chlorite.

The disproportionation products NaClO₃ and NaClO₂ would not act as an efficient oxidant in our system.

**Scheme S2.** Control experiments with PhIO **1a** prepared by classical procedure (hydrolysis with aqueous NaOH).^{S1}

These control experiments suggest that the oxidizing ability of the **1a** would depend on the preparation method.

Spectroscopic study

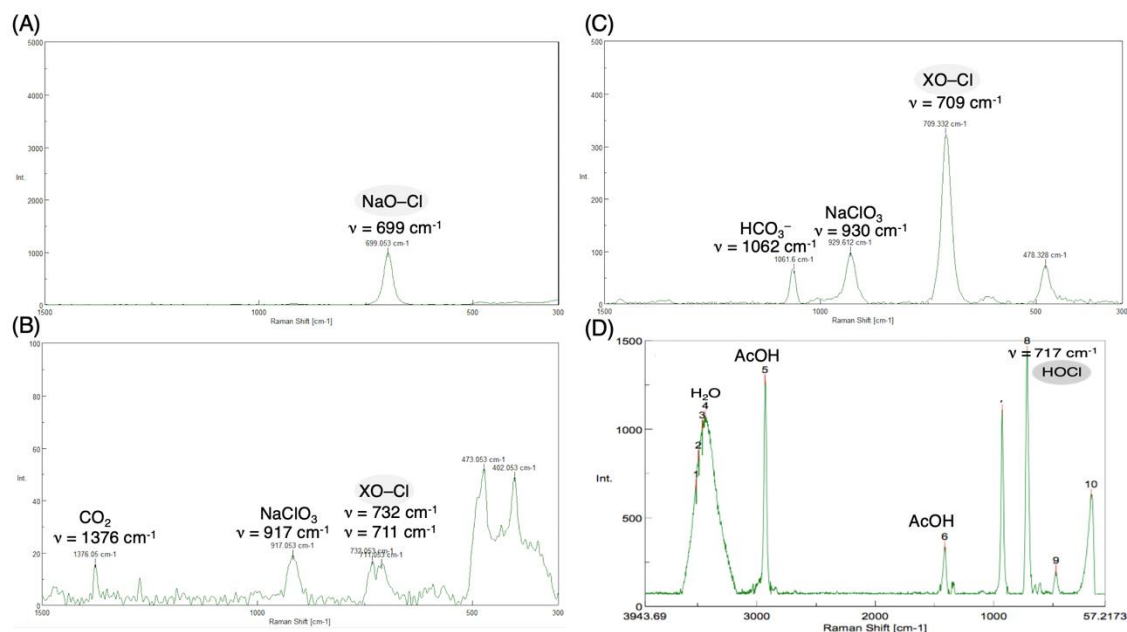
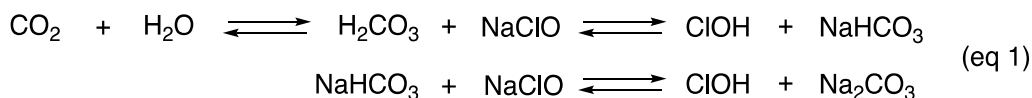
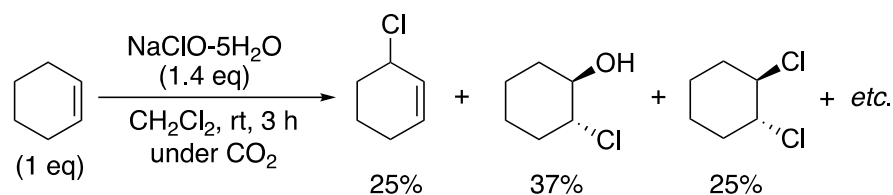


Figure S1. Raman spectra of (A) 30% aq. NaClO solution/rt/under air; (B) 30% aq. NaClO/rt/10 min/under CO₂; (C) 13% aq. NaClO and 10% aq. NaHCO₃/rt/10 min/under air; (D) NaClO-5H₂O/AcOH/rt/5 min/under air.

The Raman spectra of authentic Cl₂O were reported for either solid/gas/liquid state, in which Cl–O stretching vibration was observed in the range of $\nu = 630\text{--}690\text{ cm}^{-1}$ depending on the conditions.² In our system, a slightly blue shifted Cl–O stretching vibration was observed (conditions (B) and (C), in Figure S1), which was similar to the peak observed for NaClO-AcOH system (conditions (D)). It should be noted that the lack of carbonate/bicarbonate ions under CO₂ atmosphere (conditions (B) in Figure S1), indicating the lack of the equilibrium shown in eq 1. Further, the expected intermediate Cl₂ ($\nu = 538\text{ cm}^{-1}$) was not observed.



Reaction with NaClO-5H₂O-CO₂ (this work)



Reaction with Cl₂O (Data taken from *Can. J. Chem.* **1974**, *52*, 2573)

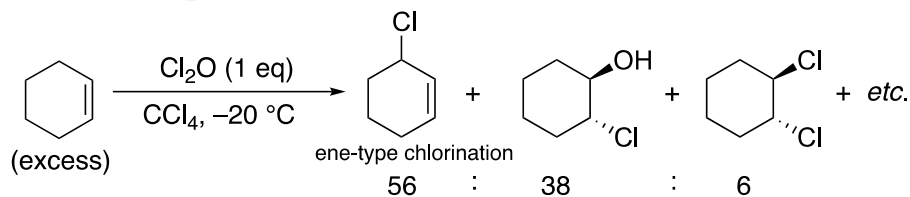


Figure S2. Trapping experiment with cyclohexene.

The products distribution of the reaction using NaClO-5H₂O under CO₂ is similar to the previously reported reaction using pure Cl₂O. The allyl chloride would be formed by ene-type chlorination of olefin with Cl₂O.^{S3}

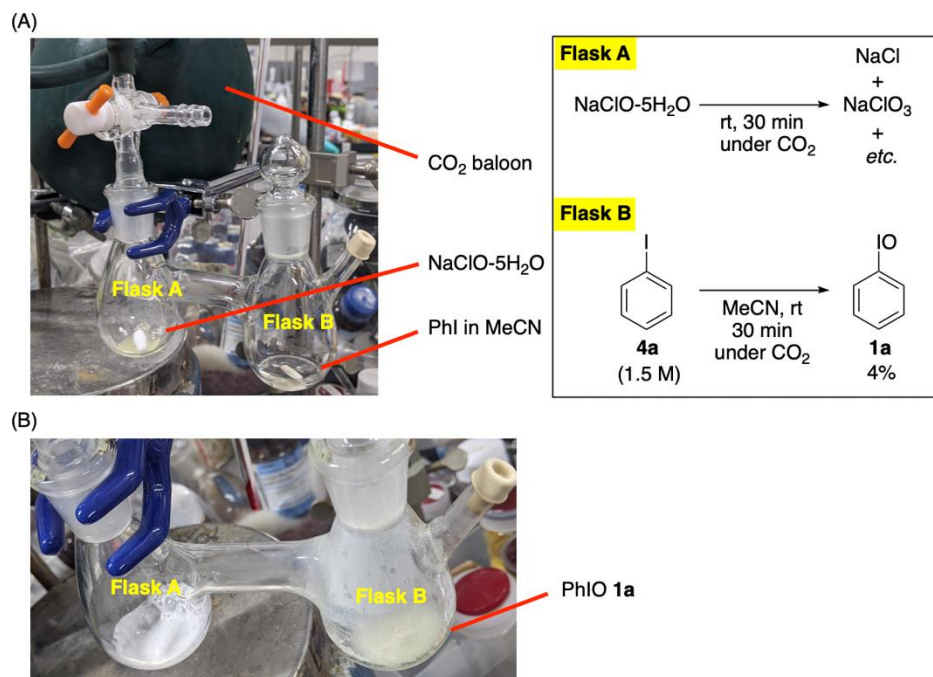


Figure S3. Appearance of (A) Connected flask experiment. (B) Reaction mixture after 30 minutes.

The gaseous species formed by the reaction of NaClO and CO₂ in Flask A was moved to Flask B, which oxidize iodobenzene **4a**. The MeCN-insoluble pale yellow precipitate in Flask B indicates the formation of iodosylbenzene **1a**. Analytical data (FT-IR, mp) of the precipitate are consistent with those of a sample obtained by our optimized reaction conditions.

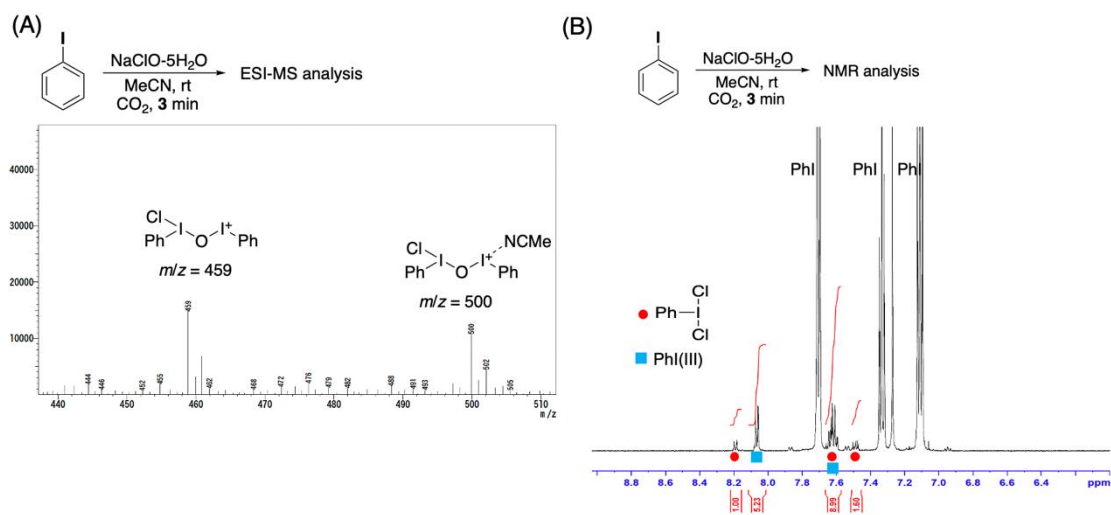


Figure S4. (A) ESI-MS spectrum (positive ion mode) of the reaction mixture (MeCN , desolvation temperature: 100°C). A weak peak attributable to $[(\text{PhIO})_3\text{Cl}]^+$ ($m/z = 679$) was also detected. (B) ^1H NMR spectrum of the reaction mixture (CDCl_3 , 500 MHz). A major peaks (filled square) attributable to hypervalent iodine(III) species disappeared after prolonged stirring at room temperature.

The presence of PhICl_2 and oligomeric μ -oxo species in an early stage of the reaction mixture was confirmed by ^1H NMR and ESI-MS analyses.

References

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2. Renard, J. J.; Bolker, I. *Chem. Rev.* **1976**, 76, 587.
3. Torii S.; Tanaka H.; Tada N.; Nagao S.; Sasaoka M. *Chem. Lett.* **1984**, 877.