Supplementary Material

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

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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 \( \nu = 630–690 \text{ cm}^{-1} \) 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.

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\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 + \text{NaClO} \rightleftharpoons \text{ClOH} + \text{NaHCO}_3 \\
\text{NaHCO}_3 + \text{NaClO} & \rightleftharpoons \text{ClOH} + \text{Na}_2\text{CO}_3
\end{align*}
\] (eq 1)
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.⁵³
Figure S3. Appearance of (A) Connected flask experiment. (B) Reaction mixture after 30 minutes.

The gaseous species formed by the reaction of NaClO and CO$_2$ 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 [(PhIO)₃Cl]⁺ (m/z = 679) was also detected. (B) ¹H NMR spectrum of the reaction mixture (CDCl₃, 500 MHz). A major peaks (filled square) attributable to hypervalent iodine(III) species disappeared after prolonged stirring at room temperature.

The presence of PhICl₂ and oligomeric μ-oxo species in an early stage of the reaction mixture was confirmed by ¹H NMR and ESI-MS analyses.
References