K₂S₂O₈-MEDIATED DIFUNCTIONALIZATION OF C≡C BONDS IN WATER: A SIMPLE AND EFFICIENT APPROACH TO α,α-DIHALOACETOPHENONES FROM PHENYLACETYLENES AND NaX

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GRAPHICAL ABSTRACT

Abstract A novel K₂S₂O₈-mediated oxy-1,1-dihalogenation of alkynes with NaX in the presence of water has been developed, affording α,α-dihaloacetophenones in moderate to good yields. The advantages of this reaction are mild reaction conditions, operational simplicity, and use of pure water as reaction medium. A plausible reaction mechanism is proposed on the basis of mechanistic studies.

Keywords α,α-Dihaloacetophenones; oxyhalogenation; persulfate salts; phenylacetylenes; water

INTRODUCTION

The transformation of alkynes is an essential functional group interconversion for organic synthesis.[1–5] The resulting compounds from alkyne functionalization take a privileged position in drug discovery, supramolecular chemistry, polymer chemistry, materials science, and biotechnology.[2] Among intensive research in alkyne chemistry, vicinal difunctionalization of alkynes involving the simultaneous installation of two different vicinal chemical bonds exemplifies a class of reactions with significant synthetic potential to rapidly increase molecular complexity.[3] In this regard, oxyhalogenation of alkynes has recently attracted attention because it installs two versatile handles (carbonyl and halide) for further structural elaboration.[4,5]
Although significant progresses have been made, some crucial issues have remained fairly unaddressed: (1) the reaction is mainly limited to either oxybromination or oxychlorination,\[4,5a\] (2) hazardous or low-atom-efficiency halogenating reagents and environmentally undesirable organic solvents are often employed,\[4,5\] and (3) special implements and transition metals are sometimes utilized.\[4b,4d,4e,5b\] Therefore, the development of new, mild, and environmentally friendly approaches for selective and direct oxidative conversion of alkynes to multifunctional organic compounds still remains a highly desirable goal in organic synthesis. Herein, we report a K$_2$S$_2$O$_8$-mediated oxy-1,1-dihalogenation of alkynes with NaX in the presence of water, which illustrates a convenient method toward simultaneous incorporation of halide and ketone group to a carbon–carbon triple bond.

$\alpha,\alpha$-Dihaloacetophenones are an important class of intermediates in organic synthesis and have been used in the synthesis of natural products and pharmaceuti-
cals.$[6]$ In general, $\alpha,\alpha$-dihaloacetophenones are mainly obtained from acetophenones with excess gaseous or volatile halogens, or their complex compounds.$[7]$ However, these methods involve the use of toxic, hazardous, or low-atom-efficiency halogenating reagents. Recently, direct conversion of alkynes to $\alpha,\alpha$-dihaloacetophenones has attracted much attention because ketones are frequently prepared from the corre-
sponding alkynes.$[8]$ Although oxidation of alkynes for the synthesis of $\alpha,\alpha$-dichloro-
acetophenones or $\alpha,\alpha$-dibromoacetophenones is documented in the literature,$[4]$ a common procedure that leads to both $\alpha,\alpha$-dichloroacetophenones and $\alpha,\alpha$-dibromoace-
tophenones is much less abundant and more limited.$[5]$ For instance, Pandit et al. reported a cationic-surfactant-mediated direct transfer of halides to alkynes to afford $\alpha,\alpha$-dihaloketones promoted by phenyliodonium diacetate.$[5a]$ Subsequently, Liu et al. described a oxy-1,1-dihalogenation of alkynes with N-halosuccinimides as the halo-
gen source using FeCl$_3$·H$_2$O as the oxidant in tetrahydrofuran (THF)–H$_2$O.$[5b]$ Recently, Madabhushi et al. reported a oxyhalogenation of terminal alkynes using an oxone–KX system in CH$_3$CN-H$_2$O.$[5c]$ However, these strategies suffer from one or more limitations, including use of expensive and low-atom-efficiency reagents and/or environmentally undesirable organic solvents and/or even transition metals. Therefore, the development of new, mild, and environmentally friendly approaches for the direct synthesis of $\alpha,\alpha$-dihaloacetophenones from phenylacetylenes still remains a highly desirable goal in organic synthesis. Herein, we present a mild and efficient method for the synthesis of $\alpha,\alpha$-dihaloacetophenones from phenylacetylenes and NaX using K$_2$S$_2$O$_8$ as the oxidant in the presence of pure water.

**RESULTS AND DISCUSSION**

In our previous studies, phenacyl bromides could be efficiently synthesized via K$_2$S$_2$O$_8$-mediated tandem hydroxybromination and oxidation of styrenes using KBr as a bromine source in the presence of water.$[9]$ We envisioned that $\alpha,\alpha$-dihaloacetophenones can be generated in a similar fashion if the styrenes are replaced with phenylacetylenes. When phenylacetylene was reacted with KBr in the presence of K$_2$S$_2$O$_8$ in H$_2$O at 60 °C for 12 h, we were delighted to see that our desired product, $\alpha,\alpha$-dibromoacetophenone, was indeed formed in 85% yield (Table 1, entry 1). The control experiment showed that K$_2$S$_2$O$_8$ was necessary for the reaction to proceed (Table 1, entry 2). Among the bromine sources screened, NaBr was found to be most
effective (Table 1, entries 3–5). When other persulfate salts, such as \( \text{Na}_2\text{S}_2\text{O}_8 \) or \( (\text{NH}_4)_2\text{S}_2\text{O}_8 \), were used in place of \( \text{K}_2\text{S}_2\text{O}_8 \), the desired product was obtained in poor yields (Table 1, entries 6 and 7). Changing the solvent to \( \text{CH}_3\text{OH–H}_2\text{O} \), \( \text{CH}_3\text{CN–H}_2\text{O} \) or \( \text{CH}_3\text{CH}_2\text{OH–H}_2\text{O} \) afforded 62–65% yield of product, whereas the use of organic solvents alone as the solvent gave no product (Table 1, entries 8–13). When the mixed solvent of other solvent–\( \text{H}_2\text{O} \) was used as the reaction medium, only the desired \( \alpha,\alpha\text{-dibromoacetophenone} \) was detected by gas chromatography (GC) and the remaining starting material decomposed in those cases, whereas organic solvents afforded \( \text{trans-1,2-dibromo-1-phenylethene} \) as the major product. Increasing the reaction temperature to \( 70^\circ\text{C} \) did not benefit the reaction (Table 1, entry 14). The reaction between phenylacetylene and \( \text{KCl} \) in the presence of \( \text{K}_2\text{S}_2\text{O}_8 \) in \( \text{H}_2\text{O} \) for 12 h provided the desired \( \alpha,\alpha\text{-dichloroacetophenone} \) in 45% yield (Table 1, entry 15). After a series of optimizations, the best yield (58%) was achieved when \( \text{NaCl} \) was used as chlorine source in the presence of \( \text{K}_2\text{S}_2\text{O}_8 \) (Table 1, entry 16). On the basis of these results, we determined the optimized conditions to be \( \text{K}_2\text{S}_2\text{O}_8 \) (2.5 equiv), \( \text{NaX} \) (2.0 equiv), \( \text{H}_2\text{O} \), 60°C, and 12 h (for details, see the supplementary

### Table 1. Optimization of the reaction conditions

| Entry | Oxidant | Halogen source | Solvent       | Yield<sup>b</sup> (%) |
|-------|---------|----------------|---------------|------------------------|
| 1     | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{H}_2\text{O} \) | 85                     |
| 2     | None    | \( \text{NaBr} \) | \( \text{H}_2\text{O} \) | 0                      |
| 3     | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{KBr} \) | \( \text{H}_2\text{O} \) | 68                     |
| 4     | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{LiBr} \) | \( \text{H}_2\text{O} \) | 75                     |
| 5     | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NH}_4\text{Br} \) | \( \text{H}_2\text{O} \) | 70                     |
| 6     | \( \text{Na}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{H}_2\text{O} \) | 74                     |
| 7     | \( (\text{NH}_4)_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{H}_2\text{O} \) | 68                     |
| 8     | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{CH}_3\text{OH–H}_2\text{O}(1/1) \) | 64                     |
| 9     | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{CH}_3\text{CN–H}_2\text{O}(1/1) \) | 65                     |
| 10    | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{EtOH–H}_2\text{O}(1/1) \) | 62                     |
| 11<sup>d</sup> | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{CH}_3\text{OH} \) | 0 (85)<sup>c</sup> |
| 12<sup>e</sup> | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{CH}_3\text{CH}_2\text{OH} \) | 0 (78)                |
| 13<sup>f</sup> | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{CH}_3\text{CN} \) | 0 (12)                |
| 14<sup>g</sup> | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaBr} \) | \( \text{H}_2\text{O} \) | 68                     |
| 15    | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{KCl} \) | \( \text{H}_2\text{O} \) | 45                     |
| 16    | \( \text{K}_2\text{S}_2\text{O}_8 \) | \( \text{NaCl} \) | \( \text{H}_2\text{O} \) | 58                     |

<sup>a</sup>Conditions: phenylacetylene (0.5 mmol), oxidant (2.5 equiv), halogen source (2.0 equiv), solvent (1 mL), 60°C, 12 h.

<sup>b</sup>Yields are determined by GC.

<sup>c</sup>The conversion is given in parentheses.

<sup>d</sup>trans-1,2-Dibromo-1-phenylethene was obtained in 42%.

<sup>e</sup>trans-1,2-Dibromo-1-phenylethene was obtained in 35%.

<sup>f</sup>trans-1,2-Dibromo-1-phenylethene was obtained in 9%.

<sup>g</sup>70°C.
material). Although phenylacetylene reacted with NaBr or NaCl in the presence of K$_2$S$_2$O$_8$ to afford the corresponding α,α-dibromoacetophenone and α,α-dichloroacetophenone, the reaction of phenylacetylene with KI did not give the corresponding α,α-diiodoacetophenone under the same reactions; instead it provided (E)-1,2-diiodophenylenethene as the main product (see Scheme S1 in the Supporting Information).

With the optimized conditions in hand, we next explored the scope of the reaction between various alkynes and NaBr, and the results are summarized in Scheme 1. Diverse phenylacetylenes bearing both electron-donating groups and electron-withdrawing groups provided the desired α,α-dibromoacetophenones in yields ranging from 61 to 78% (2a–2j). It is worth noting that F (2b), Cl (2c), and Br (2d) substituents on the phenyl ring were well tolerated, which enable potential

Scheme 1. Oxy-1,1-dibromination of alkynes with NaBr in the presence of K$_2$S$_2$O$_8$. Conditions: alkynes (0.5 mmol), K$_2$S$_2$O$_8$ (2.5 equiv), NaBr (2.0 equiv), H$_2$O (1 mL), 60 °C, 12 h. Isolated yields.
applications in further functionalization.\textsuperscript{[10]} In addition, this reaction was also applicable to internal alkynes, 1-phenyl-1-propyne, and 1-phenyl-1-butyne, as demonstrated by the formation of the desirable products in good yields (2k and 2l). While the results of phenylacetylenes were all favorable, the reaction of aliphatic alkynes did not give the corresponding \(\alpha,\alpha\)-dibromoketones; instead they afforded dibromides as the main products. For instance, when 1-heptyne was subjected to the same reaction conditions, trans-1,2-dibromo-1-heptene was obtained in 58% yield (2m).

Subsequently, we investigated the scope of the reaction with respect to alkynes and NaCl. As shown in Scheme 2, the efficiency of oxy-1,1-dichlorination is much lower than the corresponding oxy-1,1-dibromination. Phenylacetylene derivatives with electron-withdrawing substituents afforded the desired \(\alpha,\alpha\)-dichloroacetophenone in 35–49% yield (3b–3d), whereas styrene derivatives bearing electron-donating substituents provided the desired \(\alpha,\alpha\)-dichloroacetophenone in 40–46% yield (3e–3g). Notably, F (3b), Cl (3c), and Br (3d) substituents can also be tolerated in this reaction. Moreover, 1-phenyl-1-propyne and 1-phenyl-1-butyne, which are internal alkyne compounds, gave the corresponding 3h and 3i in 37 and 34% yields, respectively. Unfortunately, the reaction of 1-heptyne did not give the corresponding

\[ \text{Scheme 2. Oxy-1,1-dichlorination of alkynes with NaCl in the presence of K}_{2}\text{S}_2\text{O}_8. \text{Conditions: alkynes (0.5 mmol), K}_{2}\text{S}_2\text{O}_8 (2.5 equiv), NaCl (2.0 equiv), H}_2\text{O (1 mL), 60 °C, and 12 h. Isolated yields.} \]
α,α-dichloroketone, and only trace amounts of dichloride product (3j) were detected by NMR (see Fig. S1 in the Supporting Information).

To shed light on the mechanism of the reactions, some information has been gathered. When phenacyl chloride and bromide were introduced into the standard conditions, the desired α,α-dichloroacetophenone and α,α-dibromoacetophenone were not detected by GC [Eq. (1)]. The reaction of β-bromostyrene under the same conditions afforded only a trace amount of α,α-dibromoacetophenone [Eq. (2)]. These results indicate that phenacyl halide and β-halostyrene seem not to serve as intermediates in the reaction. Also, when the reaction was carried out in the presence of BHT (2,6-di-tert-butyl-4-methyl phenol) [Eq. (3)], which was a traditional radical scavenger, α,α-dibromoacetophenone was obtained in 82% yield, thus demonstrating that a radical pathway might not be involved in the present reaction system. Furthermore, Table 1 showed that the reaction did not proceed at all in the absence of K₂S₂O₈. This result shows that K₂S₂O₈ plays a role as the oxidant. In addition, the results that we obtained from Table 1 suggested that carbonyl oxygen of α,α-dihaloacetophenone originates from water, not from the molecular oxygen of air. Finally, the presence of the yellow color during the reaction suggests the formation of bromine.⁹

Based on these results and related reports,⁴,⁵ a plausible mechanism for the present process is proposed in Scheme 3. Initially, oxidation of the halide ion by the persulfate ion generates molecular halogen, which is trapped by water to give hypohalous acid (HOX). Next, hypohalous acid converts into dihalo monoxide (X₂O)⁵⁸,¹¹ and undergoes electrophilic addition onto the phenylacetylene to produce a three-membered cyclic halonium ion intermediate A. The cyclic intermediate undergoes ring opening by the nucleophile (XO⁻, hydroxy or halide ion) to yield the corresponding substituted products B, C, and D. This also further explained the results of Schemes 1 and 2. When substrates were aliphatic alkynes, halonium ion intermediate undergoes ring opening by halide ion to give vicinal dihalo substituted product, whereas when substrates were phenylacetylenes, halonium ion
intermediate undergoes ring opening by XO⁻ (path a) and water (path b) to provide vicinal substituted products B and C. Finally, the intermediates B and C are converted into the corresponding α,α-dihaloacetophenone.

CONCLUSIONS

In conclusion, we have developed a highly attractive and operationally simple oxy-1,1-dihalogenation method to construct α,α-dichloroacetophenones and α,α-dibromoacetophenones. This method is of great value from the viewpoint of green chemistry and organic synthesis due to use of inexpensive halogen sources, K₂S₂O₈ as oxidant, and H₂O as solvent. Further mechanistic studies and development of relevant reactions are currently under investigation.

EXPERIMENTAL

All reagents and solvent were purchased commercially and used without further purification. Mass spectra were measured on a mass instrument (EI). ¹H NMR spectra were recorded on 400 MHz in CDCl₃, and ¹³C NMR spectra were recorded on 101 MHz in CDCl₃ using Tetramethylsilane (TMS) as internal standard.
Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), and coupling constants (J) are reported in hertz. Copies of 1H NMR and 13C NMR spectra are provided as Supporting Information.

K2S2O8 (2.5 equiv.), NaX (2.0 equiv.), phenylacetylene (0.5 mmol), and H2O (1 mL) were added to a 25-mL Schlenck tube. The reaction mixture was warmed to 60°C (oil bath) and stirred for 12 h. The reaction was cooled to room temperature, and ethyl acetate (5 mL) and water (2 mL) were added. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (10 mL). The combined organic layers were dried over anhydrous Na2SO4, filtered, and concentrated. The residue was purified by column chromatography to give desired product 2,2-dibromo-1-phenylethanone 2a. Compound 2a was a pale yellow oil. 1H NMR (CDCl3, 400 MHz) δ 6.75 (s, 1 H), 7.50 (t, J = 8.0 Hz, 2 H), 7.63 (t, J = 8.0 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 2 H); 13C NMR (CDCl3, 101 MHz) δ 39.91, 129.00, 129.72, 130.84, 134.53, 186.00. The spectral data agreed with those in the literature.[5a]

FUNDING

We are grateful for the financial support from the National Natural Science Foundation of China (21372068, J1210040, J1103312) and the Presidential Scholarship for Doctoral Students, Hunan University.

SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher’s website.

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