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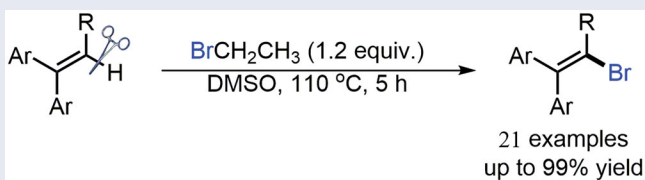
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ABSTRACT

Aliphatic bromide was used as a halogenation reagent in the presence of DMSO, resulting in 2,2-diarylviny bromides from the corresponding 1,1-diarylethylenes. This protocol not only provides a convenient and straightforward strategy for the rapid construction of various 2,2-diarylviny bromides without bromine and extra oxidants, but also can improve the atom economy of Kornblum oxidative reaction.

GRAPHICAL ABSTRACT



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KEYWORDS


Vinyl bromides;
Bromination; Bromoethane

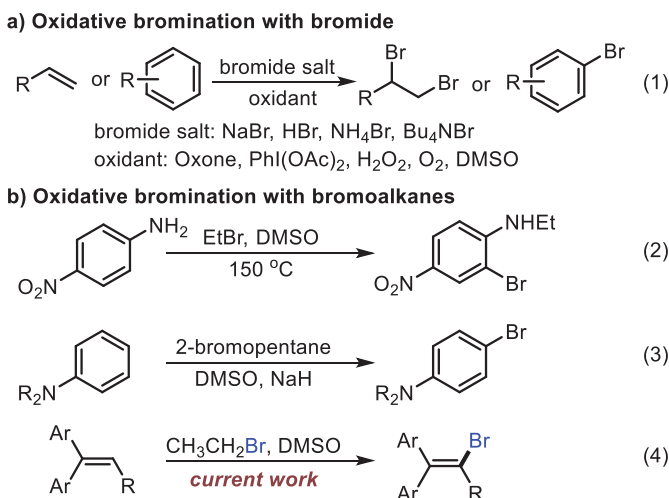
Introduction

2,2-Diarylviny bromides are privileged building blocks and can be easily converted to organic molecules bearing 2,2-diarylviny moieties, which have wide applications in organic synthesis and functional materials.^[1–10] Therefore, it is important to develop an efficient protocol for the synthesis of 2,2-diarylviny bromides. Currently, the bromination of 1,1-diarylethylenes with bromine is still the most widely used method for the synthesis of 2,2-diarylviny bromides.^[11–13] However, bromine is highly toxic and the reaction will generate hazardous HBr as a byproduct. Therefore, the green chemistry calls for the development of safe and environmentally benign bromination strategies.^[14–16] For example, Lin's group recently reported the use of *N*-bromosuccinimide (NBS) as a safer bromination reagent heated in HOAc.^[14]

Recently, synthetic chemists have developed oxidative halogenations by simulating the biological halogenation in nature, and the utilization rate of halogen atoms can be as high as 100%. Bromide salts can serve as brominating reagent in the presence of oxidants such as oxone, NaIO₄, selectfluor, PhI(OAc)₂, O₂, and H₂O₂ (Scheme 1, Eq. (1)).^[17–27] For example, Jiao's group reported the bromination of olefins using DMSO/

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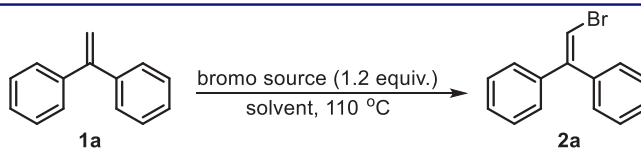


Scheme 1. Oxidative bromination of arenes and olefins.

HBr system affording dibrominated alkanes and bromohydrins.^[28–31] Zhang's group reported the use of sodium bromide as bromination reagent of quinolines in presence of copper(II) and PhI(OAc)₂.^[32] Bromination with alkyl bromide as a bromine source has also been reported in combination with dimethyl sulfoxide (DMSO). In 1956, Pan reported the first example of the bromination of aniline with ethyl bromide in DMSO (Scheme 1, Eq. (2)).^[33] In 2009, Guo also realized the bromination of anilines using 2-bromopentane and DMSO in the presence of NaH (Scheme 1, Eq. (3)).^[34] Despite the significance of these novel strategies, there are still several unsolved problems in this transformation. Direct C-H halogenation of aromatic compounds has been accomplished, however, the application of this strategy into preparation of alkenyl halides from olefins remains elusive. For olefin substrates, bromination addition products such as dibrominated alkanes and bromohydrins are resulted. Therefore, it is useful to develop a mild and environmentally friendly strategy for the direct bromination of olefins. Herein, we report a novel oxidative bromination of 1,1-diarylethylene using DMSO and bromoethane (Scheme 1, Eq. (4)).

Results and discussion

The optimized conditions were obtained by screening the two reaction parameters (bromo source and solvent) by using 1,1-diphenylethylene as a substrate. When the bromide salt such as NaBr and LiBr were used as a bromo source, no target product **2a** was yielded (entries 1 and 2, Table 1). When NBS was used as a bromination reagent, the target product **2a** was obtained in 8% yield (entry 3). When BrCH₂CO₂Et was used, the yield of **2a** increased to 59% (entry 4). To our delight, when BrCH₂CH₃ was used, 2,2-diphenylvinyl bromide (**2a**) was produced with 94% GC yield and 90% isolated yield. The solvent also plays a key impact on the results of this reaction. When toluene, CH₃CN, and *N,N*-dimethylformamide was used instead of DMSO, no bromination product **2a** was afforded (entries 6–8). These results indicated that DMSO might play a

Table 1. Optimization of reaction conditions.^{a,b}

Entry	Bromo source/solvent	Yield (%) ^b
1	NaBr/DMSO	n.r.
2	LiBr/DMSO	n.r.
3	NBS/DMSO	8
4	BrCH ₂ CO ₂ Et/DMSO	69
5	BrCH ₂ CH ₃ /DMSO	94 (90)
6	BrCH ₂ CH ₃ /Tol	n.r.
7	BrCH ₂ CH ₃ /ACN	n.r.
8	BrCH ₂ CH ₃ /DMF	n.r.
9	80 °C instead of 110 °C	70

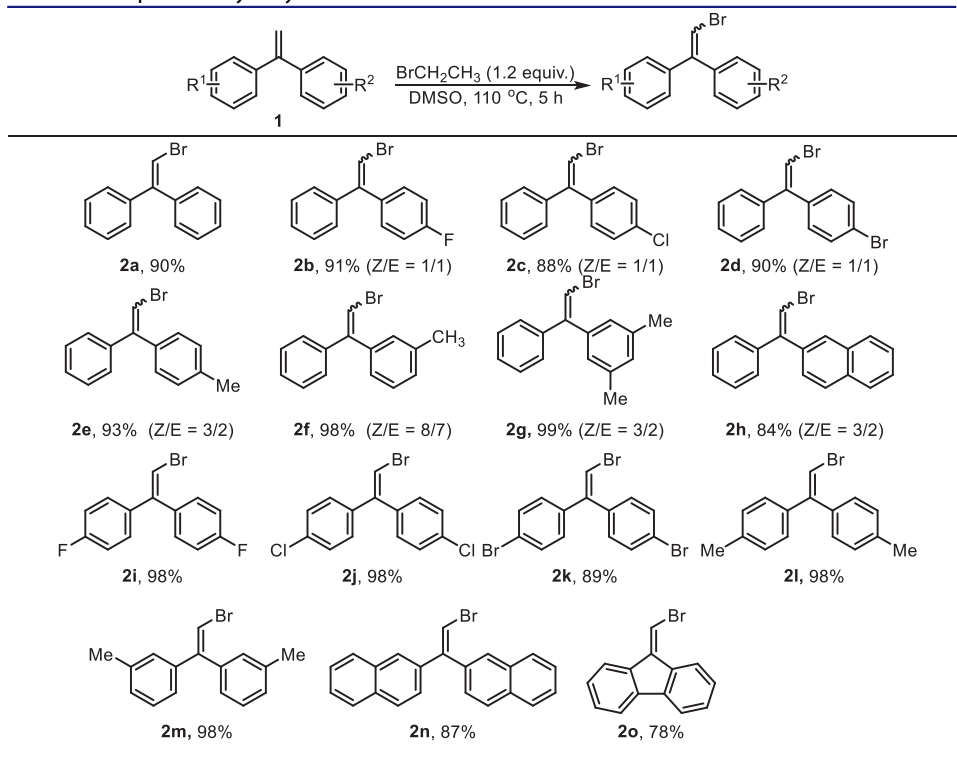
^aReaction conditions: **1a** (0.2 mmol, 1.0 equiv.), BrCH₂CH₃ (0.24 mmol, 1.2 equiv.), DMSO (0.5 mL), 110 °C, under N₂, 5 h.
^bThe yield was determined by GC analysis with mesitylene as an internal standard. The value in parentheses is the isolated yield. n.r. = no reaction.

key role in the formation of product **2a**. When we attempted to lower the temperature from 110 °C to 80 °C, the yield of **2a** decreased to 70% (entry 9). Therefore, the optimal conditions for the oxidative bromination involved treatment of 1,1-diphenylvinyl (**1a**) at 110 °C in the presence of 1.2 equiv. of BrCH₂CH₃ in DMSO (entry 5).

With the optimized conditions in hand, the scope of the bromination reactions was explored by testing a series of 1,1-diarylethylene containing different substituents on phenyl ring and the representative examples are shown in Table 2. This method exhibited good functional group compatibility and excellent chemoselectivity. The bromine atom can be selectively incorporated onto vinyl fragment instead of diaryl motifs. Satisfactory yields were obtained for the substrates in which the phenyl groups are mono- or disubstituted with either electron-donating groups (such as methyl) or electron-withdrawing groups (such as fluoro, chloro, and bromo) (**2a–2l**). When one or both of phenyl groups were replaced by naphthyl group, 2-naphthyl-2-phenyl vinyl bromide **2m** or 2,2-dinaphthyl vinyl bromide **2n** could be obtained with high yields. Interestingly, when 9-methylene-9H-fluorene was subjected to the above reaction conditions, the target product **2o** was afforded in good yield.

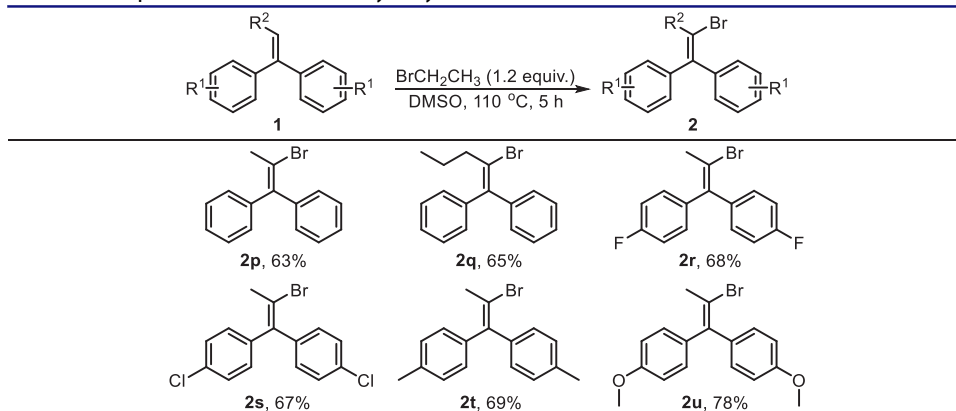
Subsequently, various tri-substituted 1,1-diarylethylene were also evaluated (Table 3), which could proceed smoothly to give the corresponding vinyl bromides in good yields (**2p–2u**). A scale-up reaction has also been performed on a gram level to demonstrate the practicability of this strategy. When **1a** (1.08 g) was subjected to the standard conditions, the desired product **2a** could be gained in 90% yield (1.40 g) (Scheme 2).

To gain some insights into the reaction mechanism, several control experiments have been carried out. When benzyl bromide was applied instead of bromoethane, the desired product **2a** were yielded with 88% yield together with 90% of benzaldehyde, which proved that Kornblum oxidation of bromoalkane by DMSO provide a convenient bromination strategy toward 1,1-diarylethylene (Scheme 3(a)). When **1a** was treated with [(DMS)Br⁺]Br⁻ in DMF at 110 °C, the desired product **2a** in 88% yield, proving that [(DMS)Br⁺]Br⁻ serve as the reactive bromo source (Scheme 3(b)).

Table 2. Scope of diarylethylene.^{a,b}

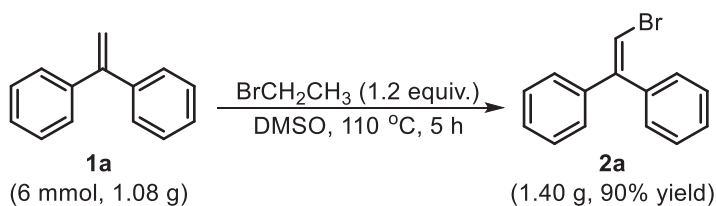
^aReaction conditions: **1a** (0.5 mmol, 1.0 equiv.), BrCH₂CH₃ (0.6 mmol, 1.2 equiv.), DMSO (0.5 mL), 110 °C, under N₂, 5 h.

^bIsolated yield.

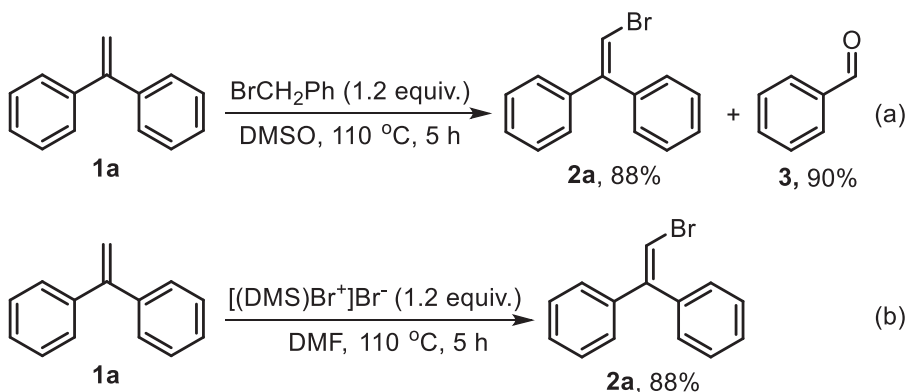
Table 3. Scope of trisubstituted diarylethylene.^{a,b}

^aReaction conditions: **1a** (0.5 mmol, 1.0 equiv.), BrCH₂CH₃ (0.6 mmol, 1.2 equiv.), DMSO (0.5 mL), 110 °C, under N₂, 5 h.

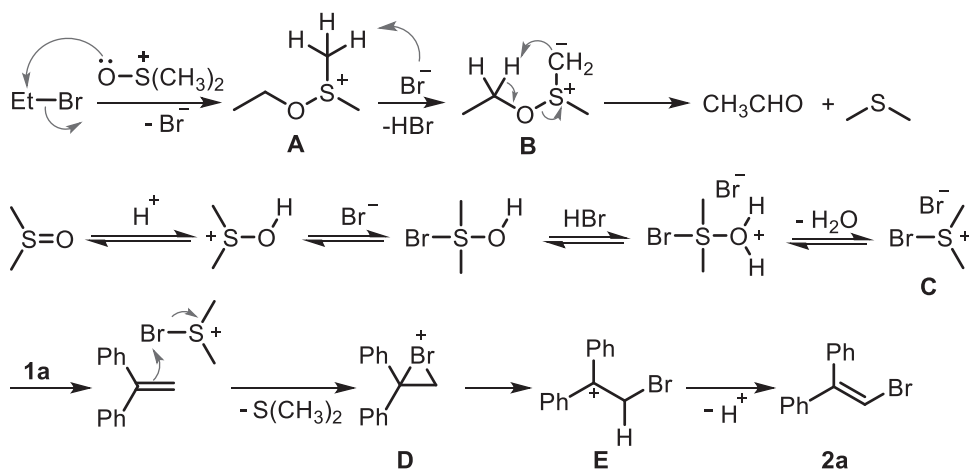
^bIsolated yield.



Scheme 2. Gram-scale experiment.



Scheme 3. Control experiments for mechanism insight.



Scheme 4. Proposed mechanism.

According to the above experimental results and previous reports,^[35–40] a plausible DMSO-mediated oxidative bromination mechanism was proposed (Scheme 4). Firstly, the reaction starts from an $\text{S}_{\text{N}}2$ reaction of bromoethane with the DMSO to form sulfonium salt **A**. Then deprotonation of **A** affords **B** and HBr, which was oxidized by DMSO to afford bromodimethylsulfonium bromide **C** according to Jiao's report.^[28–31] Meanwhile, intermediate **B** undergoes [2, 3]-rearrangement to give acetaldehyde while

releasing dimethylsulfide (DMS). The electrophilic reaction between **C** and 1,1-diphenylethylene **1a** leads to three-membered bromonium ion species **D**. Then rearrangement of **D** affords **E**, which undergoes β -H elimination to provide **2a** as the final product.

Conclusion

In summary, a novel DMSO-mediated oxidative bromination has been developed with bromoethane as the bromo source. This reaction was mild, convenient, and environmentally friendly due to the commercial availability, low cost, and air stability of bromoethane avoiding the use of bromine and extra oxidants for the synthesis of 2,2-diarylvinyl bromides, which are very important intermediates in many complex organic molecules. Further application of this strategy into organic synthesis is underway in our laboratory.

General procedure for the preparation of 2,2-diarylvinyl bromides

A solution of 1,1-diphenylethylene (**1a**) (88 μ L, 0.5 mmol) and bromoethane (45 μ L, 0.6 mmol) in DMSO (1.0 mL) in a sealed reaction tube was stirred at 110 °C (oil bath) for 5 hrs under N₂ atmosphere. The reaction was quenched with ethyl acetate and water, and then extracted with ethyl acetate (3 \times 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (petroleum ether) to give the pure product.

¹H NMR and ¹³C NMR spectra for the products are available in the [Supplementary information](#).

Disclosure statement

No potential conflict of interest was reported by the author(s).

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