JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

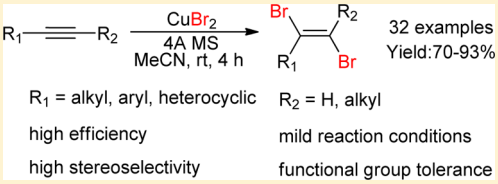
Method for Transforming Alkynes into (*E*)-Dibromoalkenes

Jiannan Xiang, Rui Yuan, Ruijia Wang, Niannian Yi, Linghui Lu, Huaxu Zou, and Weimin He*

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China

Supporting Information

ABSTRACT: The highly stereoselective bromination of alkynes has been realized by using copper(II) bromide as both the reacting partner and the catalyst, offering a generally efficient synthesis of (*E*)-dibromoalkenes. The reaction conditions are exceptionally mild, and a wide range of functional groups are well tolerated.



INTRODUCTION

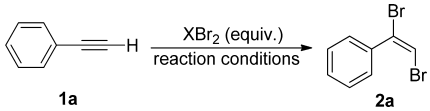
Methods for the formation of the carbon−bromine bond are important in organic synthesis.[1] Organobromine compounds containing fundamental functional groups are useful synthetic intermediates, including allyl bromide, alkyl bromide, or aryl bromide units.[2] (*E*)-1,2-Vinylic dibromides represent one particularly interesting bromine-containing functional group. They have found widespread applications in organic synthesis, biological research, and analytical chemistry.[3]

In general, the electrophilic addition of molecular bromine to alkynes is one of the common methods for the synthesis of (*E*)-dibromoalkenes.[4] However, it suffers from the use of hazardous chemicals and lack of chemoselectivity. Alternative methods for the synthesis of these bromides are the reactions of alkyne with other bromination reagents,[5] such as KBr/Selectfluor,[6] KBr/diacetoxy iodobenzene,[7] HBr/TBHP,[8] and NBS.[9] However, these methods present several limitations, such as the occurrence of side reactions, lack of stereoselectivity and low functional group tolerance. Continuing with our interest in alkyne chemistry,[10] we focused our attention on the development of a new method for the synthesis of (*E*)-dibromoalkenes. Herein we report the results of our investigation which resulted in a mild and highly stereoselective transformation of alkynes into (*E*)-dibromoalkenes in the presence of copper(II) bromide.

RESULTS AND DISCUSSION

To develop conditions that would be highly compatible with various functional groups, acidic additives and alkaline cocatalysts were avoided in the screening. In an initial study, phenylacetylene was treated with 1 equiv of $CuBr_2$ at room temperature in anhydrous acetonitrile for 4 h. Pleasingly, (*E*)-(1,2-dibromovinyl) benzene **2a** was observed in 56% yield based on NMR analysis (Table 1, entry 1). Attempts to increase the reaction efficiency were tried using different metal bromides, and this study showed that $CuBr_2$ was the best reagent (Table 1, entries 2−6). Excitingly, when the loading of $CuBr_2$ was increased to 2 equiv, the yield of **2a** was improved to 92% yield from NMR analysis (Table 1, entries 7−9). In the next optimization step we screened different solvents (Table 1, entries 10−17). None of the other anhydrous solvents was superior to acetonitrile. These results prompted us to consider that the acetonitrile may be critical to this reaction.[11] Moreover, the addition of 4 Å molecular sieves (MS) resulted in an improvement of yield as otherwise ketone products may be

Table 1. Optimization of the Reaction Conditions[a]



1a 2a

entry	catalyst (equiv)	solvent	temperature	yield (%)[b,c]
1	$CuBr_2$ (1.0)	CH_3CN	rt	56
2	$FeBr_3$ (1.0)	CH_3CN	rt	25
3	$FeBr_2$ (1.0)	CH_3CN	rt	–
4	$MgBr_2$ (1.0)	CH_3CN	rt	–
5	$ZnBr_2$ (1.0)	CH_3CN	rt	–
6	$AlBr_3$ (1.0)	CH_3CN	rt	–
7	$CuBr_2$ (1.5)	CH_3CN	rt	76
8	$CuBr_2$ (2.0)	CH_3CN	rt	92
9	$CuBr_2$ (2.5)	CH_3CN	rt	92
10	$CuBr_2$ (2.0)	MeOH	rt	36
11	$CuBr_2$ (2.0)	THF	rt	57
12	$CuBr_2$ (2.0)	DMF	rt	46
13	$CuBr_2$ (2.0)	DMSO	rt	40
14	$CuBr_2$ (2.0)	acetone	rt	21
15	$CuBr_2$ (2.0)	CH_2Cl_2	rt	–
16	$CuBr_2$ (2.0)	1,4-dioxane	rt	–
17	$CuBr_2$ (2.0)	toluene	rt	13
18[d]	$CuBr_2$ (2.0)	CH_3CN	rt	97(93)
19	$CuCl_2$ (2.0)	CH_3CN	rt	–

[a]All reactions were performed with phenylacetylene (0.1 mmol), metal salts, and anhydrous solvent (0.5 mL). [b]Estimated by ^1H NMR spectroscopy using diethyl phthalate as an internal reference. [c]The number in parentheses refers to the yield of isolated product. [d]5 mg 4 Å molecular sieves was added to the reaction mixture.

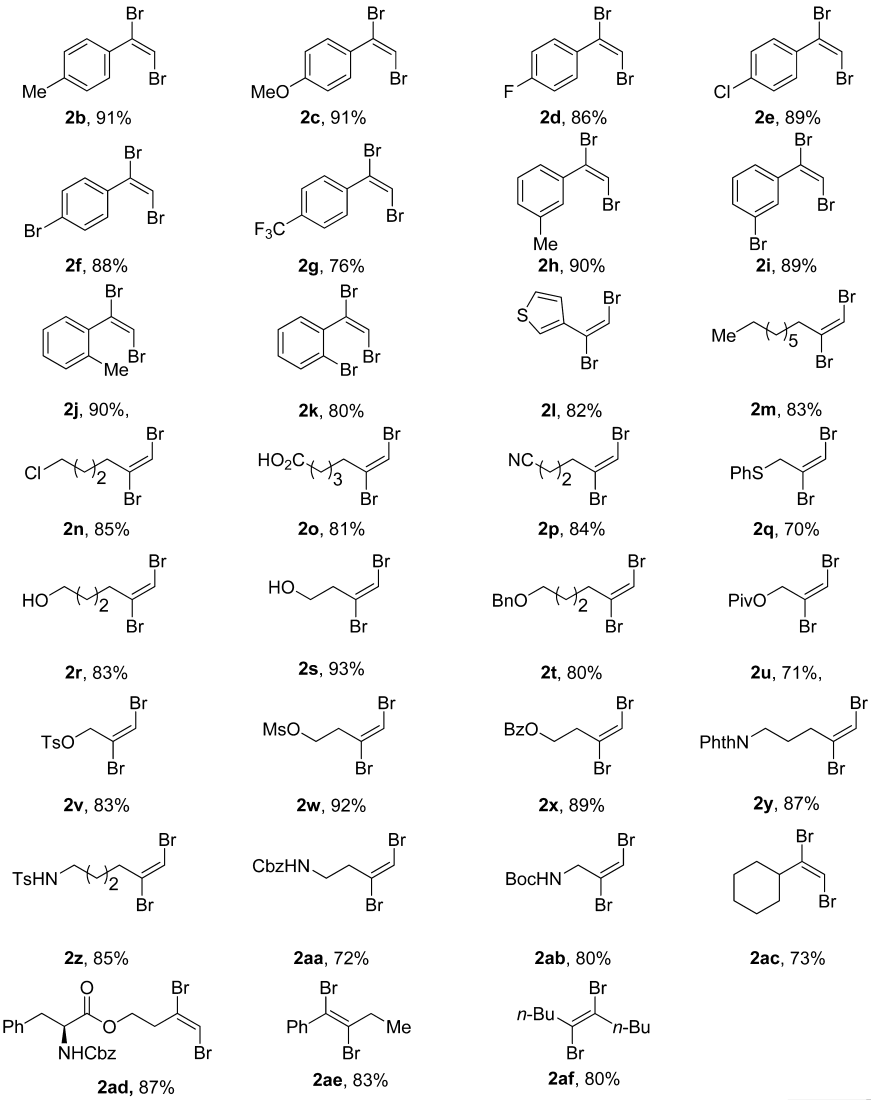
Received: August 2, 2014
Published: November 19, 2014

   dx.doi.org/10.1021/jo501776b | J. Org. Chem. 2014, 79, 11378−11382

Table 2. Reaction Scope[a]

1 2

R_1 = alkyl,aryl,heterocyclic R_2 = H, alkyl



[a][1] = 0.1 M.

produced in small amounts by the trace amount of water. No chlorination product was obtained in the presence of copper(II) chloride (Table 1, entry 19).

Under the optimized reaction conditions, we embarked on the evaluation of the substrate scope for this transformation (Table 2). Distinct reactivities were observed with different alkynes. First, a series of aromatic alkynes were tested and the corresponding products were furnished in good to excellent yields. The electronic effect of substituents at the para position of the aryl acetylene was evaluated (**2b**–**g**). The reaction tolerated both electron-donating and electron-withdrawing groups. Aromatic alkynes with substituents at meta (**2h**–**i**) and ortho (**2j**–**k**) positions also worked well, although giving slightly lower yields. Electron-rich heterocycle-containing alkynes (**2l**) were also suitable substrates for this transformation. However, electron-poor alkynes, such as 2- and 3-pyridylacetylenes, did not undergo the reaction, likely caused by the low reactivity of the C–C triple bonds. To further exploit the generality of this catalytic reaction, aliphatic terminal alkynes were also investigated. Aliphatic alkynes generally led to the corresponding products in good yield. Many synthetically important functional groups were readily tolerated, including an alkyl (**2m**), an alkyl chloride (**2n**), a free carboxylic acid moiety (**2o**), a nitrile (**2p**), an oxidizable PhS group (**2q**), an unprotected/protected OH (**2r**–**x**), a protected amino group (**2y**–**ab**), and a cyclohexyl (**2ac**). Notably, alkyne conjugated with L-phenylalanine was smoothly brominated to give corresponding (*E*)-dibromoethene (**2ad**) in 87% yield under our standard conditions. The internal alkyne, which was usually much less reactive than the terminal alkyne, was also tested. To our delight, 1-phenyl-1-butyne and 5-decyne could proceed smoothly, giving 83% and 80% yield and absolute stereoselectivity for **2ae** and **2af**, respectively. However, our attempt on diphenylacetylene resulted in no reaction. When 2-octene

dx.doi.org/10.1021/jo501776b | J. Org. Chem. 2014, 79, 11378–11382

(cis- and trans-mixture) was used, the expected dibromoalkane was not formed; instead, an unknown product was formed which was hard to characterize.

We also explored the reactivity of the $CuBr_2$-catalyzed dibromination system for larger-scale synthesis shown in Scheme 1. The reaction with 1.5 mmol of phenylacetylene

Scheme 1. Gram-Scale Dibromination of Phenylacetylene (1a)

n	*yield*
1.5	*93%, 0.365g*
5	*90%, 1.18g*
10	*87%, 2.28g*

produced excellent yield (93%). In the case of a 5 mmol scale reaction, a yield of 90% was obtained. The bromination proceeded smoothly even with a further increased amount of substrate (10 mmol), affording (*E*)-(1,2-dibromovinyl)benzene in 87% yield. These excellent results showed the promise of the catalytic system for large-scale synthesis in the process of alkyne bromination.

To probe the mechanism of this reaction, the copper(II)-catalyzed competitive bromination reactions of para-substituted ethynylbenzene derivatives were carried out. The reactivity order for ethynylbenzene derivatives is as follows: *p*-OMe (k_X/k_H = 2.23) > *p*-Me (1.66) > *p*-H (1.0) > *p*-F (0.83) > *p*-Cl (0.51) > *p*-Br (0.50) > *p*-CF_3 (0.19).[12] As shown in Figure 1, a

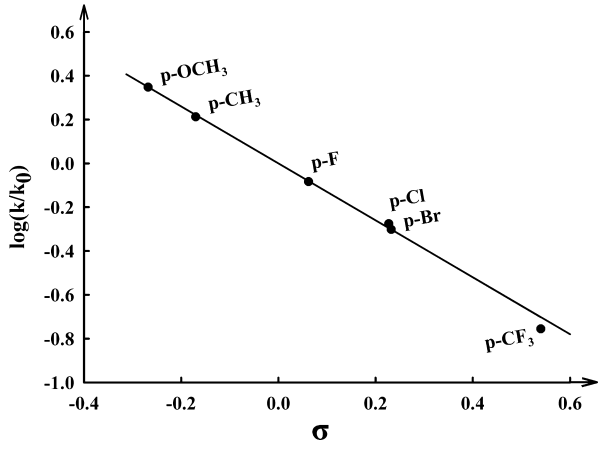
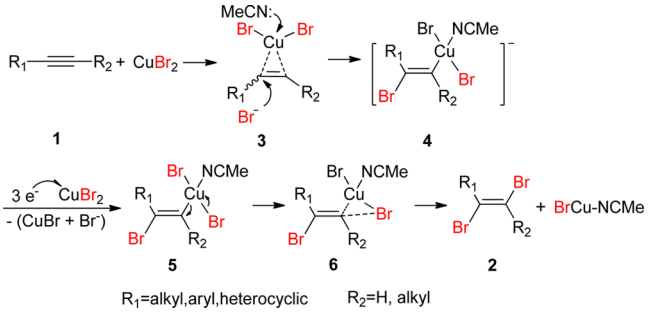


Figure 1. Hammett plot.

linear correlation with a slope of −1.3 was observed. This negative value suggests that the bromination likely proceeds via a positively charged transition state, with the positive charge on the π-complex adjacent to the phenyl ring.

Next, a possible mechanism for the synthesis of (*E*)-dibromoalkenes base on the above obtained results and the previous reports[11] is proposed. As shown in Scheme 2, a paramagnetic π-complex **3** is formed from copper(II) bromide and the alkyne. Bromide ion displaces the copper on carbon as a molecule of solvent coordinates at the copper to give the square planar Cu(II)-anion **4**. The latter transfers an electron to Cu^{II}–Br_2 to yield the neutral copper species **5**, $Cu^{I}Br$, and 1

Scheme 2. Proposed Mechanism for Dibromination of Alkynes



equiv of bromide ion. Reductive elimination through the neutral transition state **6** provides the *trans*-dibromide and a second equivalent of $Cu^{I}Br$ coordinated to solvent. In 1986, Mitsuo et al.[13] reported a similar bromination of alkynes to a mixture of acetylene bromide, (*E*)-dibromoalkene, and (*E*)-tribromoalkene using alumina-supported $CuBr_2$ (5 equiv) in carbon tetrachloride, and it is reasonable to consider that the bromination reaction has two key intermediates, δ-complex (copper(I) acetylide intermediate) and π-complex **3**.

CONCLUSIONS

In summary, we have established a facile and highly stereoselective method to synthesize (*E*)-dibromoalkenes by copper-catalyzed dibromination of alkynes. The presented methodology delivers an attractive alternative to classical procedures, as nonstereospecific, low functional group compatibility, and environmental problems can be circumvented. Various functional groups were tolerated in this method, and all the bromination products could be obtained in good to excellent yields. Due to the ready availability of the starting materials and the relatively low cost of the copper salt, this method provides a simplified way to synthesize these important (*E*)-dibromo alkenes.

EXPERIMENTAL SECTION

General Information. Commercially available reagents were of reagent grade (AR grade) and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle precoated silica gel plates. Flash column chromatography was performed over silicycle silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra were obtained using GCT-TOF instrument with EI or ESI source.

General Procedure. $CuBr_2$ (134 mg, 0.6 mmol) was added to a solution of alkynes (0.30 mmol) **1** and 15 mg of 4 Å molecular sieves in acetonitrile (1.5 mL) at room temperature. The reaction mixture was stirred at room temperature, and the progress of the reaction was monitored by TLC. The reaction typically took 4 h. Upon completion, the mixture was concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired products **2**.

*(E)-(1,2-Dibromovinyl)benzene (**2a**).* Colorless oil (71.53 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.52 (m, 2H), 7.44−7.38 (m, 3H), 6.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 129.4, 129.1, 128.2 121.3, 103.0. The data match those of the literature report.[1]

*(E)-1-(1,2-Dibromovinyl)-4-methylbenzene (**2b**).* Light yellow oil (75.35 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 6.77 (s, 1H), 2.38 (s, 3H). ^{13}C

dx.doi.org/10.1021/jo501776b | J. Org. Chem. 2014, 79, 11378−11382

NMR (100 MHz, $CDCl_3$): δ 139.6, 134.1, 129.1, 128.9, 121.6, 102.4, 21.4. The data match those of the literature report.[5b]

(E)-1-(1,2-Dibromovinyl)-4-methoxybenzene (**2c**). Light yellow oil (79.71 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.8 Hz, 2H), 6.94 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 131.1, 130.9, 129.1, 113.9, 107.0, 55.4; IR (neat): 3052, 2832, 1563, 1466, 742, 680, 575 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_9H_8Br^{81}BrO$: 291.8921; found: 291.8915.

(E)-1-(1,2-Dibromovinyl)-4-fluorobenzene (**2d**). Yellow oil (72.24 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.4 Hz, 5.2 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{C-F} = 249.3 Hz), 133.0 (d, *J* = 3.7 Hz), 131.3 (d, *J* = 8.8 Hz), 120.2, 115.4 (d, *J* = 21.9 Hz), 103.4; IR (neat): 3021, 1580, 1459, 1179, 702, 670 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_8H_5Br^{81}Br$ F: 279.8722; found: 279.8719.

(E)-1-Chloro-4-(1,2-dibromovinyl)benzene (**2e**). Colorless oil (79.03 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.45 (m, 2H), 7.39−7.36 (m, 2H), 6.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 135.3, 130.5, 128.5, 120.0, 103.7. IR (neat): 3079, 1571, 1469, 735, 702, 670 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_8H_5Br^{81}Br^{35}Cl$: 295.8426; found: 295.8421. The data match those of the literature report.[14]

(E)-1-Bromo-4-(1,2-dibromovinyl)benzene (**2f**). Yellow oil (89.76 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 131.5, 130.7, 123.6, 120.0, 103.7; IR (neat): 3083, 1568, 1423, 769, 742, 696 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_8H_5Br_2{}^{81}Br$: 339.7921; found: 339.7918.

(E)-1-(1,2-Dibromovinyl)-4-(trifluoromethyl)benzene (**2g**). Yellow oil (75.24 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (q, *J* = 8.0 Hz, 4H), 6.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 131.2 (q, J_{C-F} = 32.8 Hz), 129.6, 125.4 (J_{C-F} = 3.7 Hz), 122.3, 119.4, 104.7; IR (neat): 3020, 1688, 1331, 1138, 829, 720, 607 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_9H_5Br^{81}BrF_3$: 329.8690; found: 329.8688.

(E)-1-(1,2-Dibromovinyl)-3-methylbenzene (**2h**). Yellow oil (74.52 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.24 (m, 3H), 7.17 (d, *J* = 6.4 Hz, 1H), 6.78 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 138.0, 136.9, 130.2, 129.6, 128.1, 126.1, 121.5, 102.8, 21.3; IR (neat): 3059, 2923, 1608, 1518, 712, 668, 560 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_9H_8Br^{81}Br$: 275.8972; found: 275.8970.

(E)-1-Bromo-3-(1,2-dibromovinyl)benzene (**2i**). Yellow oil (90.78 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 1H), 7.45−7.42 (m, 1H), 7.39−7.37 (m, 1H), 7.22−7.19 (m, 1H), 6.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 132.4, 132.0, 129.8, 127.8, 122.1, 119.4, 104.3; IR (neat): 3083, 1565, 1466, 787, 742, 696 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_8H_5Br_2{}^{81}Br$: 339.7921; found: 339.7918.

(E)-1-(1,2-Dibromovinyl)-2-methylbenzene (**2j**). Yellow oil (74.52 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.23 (m, 4H), 6.85 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 135.8, 130.4, 129.4, 128.5, 126.1, 120.9, 105.1, 19.1; IR (neat): 3057, 2918, 1589, 1487, 738, 668, 560 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_9H_8Br^{81}Br$: 275.8972; found: 275.8969.

(E)-1-Bromo-2-(1,2-dibromovinyl)benzene (**2k**). Yellow oil (81.6 mg, 80% yield); ^{1}H NMR (400 MHz, CDCl3) δ 7.64 (d, *J* = 8.0, 1H), 7.38 (t, *J* = 7.4, 1H), 7.31−7.23 (m, 2H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, CDCl3): δ 138.4, 133.2, 130.7, 130.3, 127.7, 122.1, 119.5, 107.0. The data match those of the literature report.[5b]

(E)-3-(1,2-Dibromovinyl)thiophene (**2l**). Yellow oil (65.93 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.28−7.26 (m, 1H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 128.4, 128.0, 125.1, 116.3, 101.8; IR (neat): 3073, 1408, 1256, 834, 714, 625 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_6H_4Br^{81}Br$ S: 267.8380; found: 267.8378.

(E)-1,2-Dibromodec-1-ene (**2m**). Yellow oil (74.20 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.59−1.54 (m, 2H), 1.34−1.28 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.0, 102.1, 36.8, 31.8, 29.3, 29.2, 28.4, 27.0, 22.6, 14.1. The data match those of the literature report.[15]

(E)-1,2-Dibromo-5-chloropent-1-ene (**2n**). Yellow oil (70.38 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H), 1.84−1.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.9, 102.9, 44.5, 35.9, 31.0, 24.3; IR (neat): 3084, 2929, 2859, 1461, 783, 721, 696 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_6H_9Br^{81}Br$ Cl: 275.8739; found: 275.8735.

(E)-5,6-Dibromohex-5-enoic Acid (**2o**). Yellow oil (69.49 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 2.63 (t, *J* = 6.6 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H), 1.70−1.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 126.0, 102.8, 36.4, 33.7, 26.3, 23.2; IR (neat): 3298, 3089, 2947, 2871, 1752, 937, 721, 644 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_7H_{10}Br^{81}BrO_2$: 285.9027; found: 285.9023.

(E)-5,6-Dibromohex-5-enenitrile (**2p**). Yellow oil (63.75 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (s, 1H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 6.8 Hz, 2H), 2.01−1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6, 118.9, 104.6, 35.6, 23.1, 15.9; IR (neat): 3063, 2938, 2856, 2249, 698, 608 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_6H_7Br^{81}BrN$: 252.8925; found: 252.8922.

(E)-(2,3-Dibromoallyl)(phenyl)sulfane (**2q**). Yellow oil (64.68 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.31−7.28 (m, 3H), 6.45 (s, 1H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 133.0, 128.9, 127.9, 122.5, 105.3, 41.8; IR (neat): 3073, 2921, 1579, 1478, 746, 691, 618 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_9H_8Br^{81}Br$ S: 307.8693; found: 307.8690.

(E)-4,5- Dibromopent-4-en-1-ol (**2r**). Yellow oil (64.24 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (s, 1H), 3.65 (t, *J* = 6.2 Hz, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 1.68−1.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.4, 102.5, 62.3, 36.4, 31.2, 23.3; IR (neat): 3316, 3084, 2929, 2861, 1066, 694, 634 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_6H_{10}Br^{81}Br$ O: 257.9078; found: 257.9075.

(E)-3,4-Dibromobut-3-en-1-ol (**2s**). Yellow oil (63.89 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 1H), 3.86 (t, *J* = 6.0, 2H), 2.88 (t, *J* = 5.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.5, 104.7, 59.7, 40.0; IR (neat): 3315, 3086, 2930, 1059, 698, 640 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_4H_6Br^{81}Br$ O: 229.8765; found: 229.8760.

(E)-(((5,6-Dibromohex-5-en-1-yl)oxy)methyl)benzene (**2t**). Yellow oil (83.52 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.4 Hz, 4H), 7.31−7.27 (m, 1H), 6.42 (s, 1H), 4.52 (s, 2H), 3.51 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 1.71−1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 128.4, 127.6, 127.5, 126.6, 102.5, 72.9, 69.8, 36.5, 28.4, 23.8; IR (neat): 3054, 2936, 1569, 1478, 1156, 706, 632 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{16}Br^{81}Br$ O: 347.9547; found: 347.9541.

(E)-2,3-Dibromoallyl Pivalate (**2u**). Yellow oil (63.9 mg, 71% yield); ^{1}H NMR (400 MHz, CDCl3) δ 6.67 (s, 1H), 4.92 (s, 1H), 1.25 (s, 9H) ^{13}C NMR (100 MHz, CDCl3): δ 177.8, 120.1, 106.6, 64.1, 38.8, 27.1; IR (neat): 3074, 2956, 1716, 1288, 717, 686 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_8H_{12}Br^{81}Br$ O_2: 299.9184; found: 299.9188.

(E)-2,3-Dibromoallyl 4-Methylbenzenesulfonate (**2v**). Yellow oil (92.13 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 1H), 4.88 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ145.3, 132.5, 129.8, 128.1, 117.0, 109.4, 69.3, 21.6; IR (neat): 3039, 2919, 1598, 1497, 1198, 693, 562 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_{10}Br^{81}Br$ O_3S: 369.8697; found: 369.8693.

(E)-3,4-Dibromobut-3-en-1-yl Methanesulfonate (**2w**). Yellow oil (85.01 mg, 92% yield); ^{1}H NMR (400 MHz,$CDCl_3$): δ 6.63 (s, 1H), 4.42 (t, *J* = 6.0, 2H), 3.06 (t, *J* = 5.6, 2H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.8, 106.2, 65.6, 37.4, 36.7; IR (neat): 3082, 2969, 2938, 702, 525 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_5H_8Br^{81}Br$ O_3S: 307.8540; found: 307.8534.

(E)-3,4-Dibromobut-3-en-1-yl Benzoate (**2x**). Yellow oil (89.18 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6, 2H), 7.56 (t, *J* = 6.8, 1H), 7.44 (t, *J* = 7.6, 2H), 6.59 (s, 1H), 4.53 (t, *J* = 6.2, 2H), 3.09 (t, *J* = 6.2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 133.0, 129.8, 129.7, 128.3, 121.7, 105.1, 61.3, 36.6; IR (neat): 3063, 2921, 1721, 1536, 1204, 736, 602 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{11}H_{10}Br^{81}Br$ O_2: 333.9027; found: 333.9031.

(E)-2-(4,5-Dibromopent-4-en-1-yl)isoindoline-1,3-dione (**2y**). colorless solid (97.35 mg, 87% yield); mp 102−104 °C; ^{1}H NMR (400

dx.doi.org/10.1021/jo501776b | J. Org. Chem. 2014, 79, 11378−11382

MHz, $CDCl_3$) δ 7.84−7.82 (m, 2H), 7.71−7.70 (m, 2H), 6.42 (s, 1H), 3.71 (t, J = 7.4 Hz, 2H), 2.66 (t, J = 7.4 Hz, 2H), 2.00−1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 133.9, 132.0, 124.9, 123.2, 103.2, 36.8, 34.5, 26.0; IR (neat): 3094, 2964, 1707, 1510, 1465, 723, 691, 532 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{11}Br^{81}Br\ NO_2$: 372.9136; found: 372.9133.

(E)-N-(5,6-Dibromohex-5-en-1-yl)-4-methylbenzenesulfonamide (**2z**). Yellow oil (104.8 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.37 (s, 1H), 4.90 (t, J = 6.2 Hz, 1H), 2.95 (q, J = 6.8 Hz, 2H), 2.52 (t, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.59−1.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.8, 129.7, 127.0, 125.9, 102.8, 42.8, 36.1, 28.0, 23.9, 21.5; IR (neat): 3321, 3041, 2919, 2860, 1587, 1465, 686, 564 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{17}Br^{81}Br\ NO_2S$: 410.9326; found: 410.9323.

(E)-Benzyl (3,4-Dibromobut-3-en-1-yl)carbamate (**2aa**). Yellow oil (78.41 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.31 (m, 5H), 6.52 (s, 1H), 5.11 (s, 2H), 3.44 (t, J = 6.2, 2H), 2.84 (t, J = 6.2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 136.3, 128.4, 128.1, 128.0, 122.9, 104.9, 66.7, 38.4, 37.2; IR (neat): 3345, 3081, 2937, 1521, 701, 630 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{13}Br^{81}Br\ NO_2$: 362.9293;found: 362.9289.

(E)-tert-Butyl (2,3-Dibromoallyl)carbamate (**2ab**). Yellow oil (75.6 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (s, 1H), 4.89 (bs, 1H), 4.18 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ155.6, 123.3, 104.2, 80.0, 44.5, 28.3; IR (neat): 3348, 3079, 2981, 1716, 1269, 709, 628 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{13}Br^{81}Br\ NO_2$: 314.9293; found: 314.9290.

(E)-(1,2-Dibromovinyl)cyclohexane (**2ac**). Yellow oil (58.69 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 1H), 2.87−2.80 (m, 1H), 1.82−1.17 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 100.0, 42.9, 30.4, 25.5; IR (neat): 3065, 2928, 2853, 1460, 686, 560 cm^{-1}; HRMS (EI) m/z calcd for $C_8H_{12}Br^{81}Br$: 267.9285; found: 267.9282.

(E)-3,4-Dibromobut-3-en-1-yl 2-(((benzyloxy)carbonyl)amino)-3-phenylpropanoate (**2ad**). Yellow oil (133.37 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.14 (m, 8H), 7.03−7.01 (m, 2H), 6.41 (s, 1H), 5.21 (d, J = 8.4, 1H), 4.99(s, 2H), 4.59(q, J = 6.0, 1H), 4.21−4.18 (m, 2H), 3.04−2.99 (m, 2H), 2.82−2.77 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 155.5, 136.1, 135.6, 129.2, 128.5, 128.4, 128.0, 127.9, 127.0, 121.0, 105.4, 66.8, 61.7, 54.7, 38.0, 36.2

(E)-(1,2-Dibromobut-1-en-1-yl)benzene (**2ae**). Light yellow oil (72.2 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 5H), 2.83 (q, J = 7.4 Hz, 2H), 1.20 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 140.8, 129.1, 128.5, 128.2, 124.8, 115.6, 35.1, 12.1. The data match those of the literature report.[9]

(E)-5,6-Dibromodec-5-ene (**2af**). Colorless oil (71.5 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (t, J = 7.6 Hz, 4H), 1.59−1.51 (m, 4H), 1.39−1.30 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 121.6, 40.5, 29.6, 21.7, 13.9. The data match those of the literature report.[9]

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **2a**−**af**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wmhe@hnu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (no. 21302048 and no. 21271070), Specialized Research Fund for the Doctoral Program of Higher Education (no. 20130161120035), China Postdoctoral Science Foundation (no. 2013M540625), Hunan Provincial Natural Science Foundation of China (no. 4JJ7028), and the Fundamental Research Funds for the Central Universities.

■ REFERENCES

(1) Adimurthy, S.; C. Ranu, B.; Ramachandraiah, G.; Ganguly, B.; K. Ghosh, P. *Curr. Org. Chem.* **2013**, *10*, 864.

(2) Ioffe, D.; Kampf, A. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: New York, 2000.

(3) (a) De Laet, M.; Tilquin, B. *Talanta* **1992**, *39*, 769. (b) Bayatyan, R.; Bayatyan, B.; Saakyan, L. *Russ. J. Appl. Chem.* **2006**, *79*, 1849. (c) Yang, Y.; Zhang, X.; Liang, Y. *Tetrahedron Lett.* **2012**, *53*, 6557. (d) Schuh, K.; Glorius, F. *Synthesis* **2007**, 2297. (e) Karim, A. K.; Armengol, M.; Joule, J. A. *Heterocycles* **2002**, *55*, 2139. (f) Pilli, R. A.; Robello, L. G. *J. Brazilian Chem. Soc.* **2004**, *15*, 938.

(4) Eissen, M.; Lenoir, D. *Chem.—Eur. J.* **2008**, *14*, 9830.

(5) (a) Kawakami, K.; Tsuda, A. *Chem.—Asian J.* **2012**, *7*, 2240. (b) Adimurthy, S.; Ghosh, S.; Patoliya, P. U.; Ramachandraiah, G.; Agrawal, M.; Gandhi, M. R.; Upadhyay, S. C.; Ghosh, P. K.; Ranu, B. C. *Green Chem.* **2008**, *10*, 232. (c) Schmidt, R.; Stolle, A.; Ondruschka, B. *Green Chem.* **2012**, *14*, 1673. (d) Kavala, V.; Naik, S.; Patel, B. K. *J. Org. Chem.* **2005**, *70*, 4267.

(6) Ye, C.; Shreeve, J. n. M. *J. Org. Chem.* **2004**, *69*, 8561.

(7) Das, B.; Srinivas, Y.; Sudhakar, C.; Damodar, K.; Narender, R. *Synth. Commun.* **2009**, *39*, 220.

(8) Barhate, N. B.; Gajare, A. S.; Wakharkar, R. D.; Bedekar, A. V. *Tetrahedron* **1999**, *55*, 11127.

(9) Liu, J.; Li, W.; Wang, C.; Li, Y.; Li, Z. *Tetrahedron Lett.* **2011**, *52*, 4320.

(10) (a) Ye, L.; He, W.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 8550. (b) He, W.; Li, C.; Zhang, L. *J. Am. Chem. Soc.* **2011**, *133*, 8482. (c) Ye, L.; He, W.; Zhang, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 3236. (d) He, W.; Xie, L.; Xu, Y.; Xiang, J.; Zhang, L. *Org. Biomol. Chem.* **2012**, *10*, 3168. (e) Wu, C.; Huang, W.; He, W.; Xiang, J. *Chem. Lett.* **2013**, *42*, 1233. (f) Wu, C.; Liang, Z.; Yan, D.; He, W.; Xiang, J. *Synthesis* **2013**, *45*, 2605. (g) Wu, C.; Liang, Z.-W.; Xu, Y.-Y.; He, W.-M.; Xiang, J.-N. *Chin. Chem. Lett.* **2013**, *24*, 1064. (h) Xie, L.; Liang, Z.; Yan, D.; He, W.; Xiang, J. *Synlett* **2013**, *24*, 1809. (i) Xie, L.; Wu, Y.; Yi, W.; Zhu, L.; Xiang, J.; He, W. *J. Org. Chem.* **2013**, *78*, 9190. (j) Huang, W.; Xiang, J.; He, W. *Chem. Lett.* **2014**, *43*, 893. (k) Xie, L.; Yuan, R.; Wang, R.; Peng, Z.; Xiang, J.; He, W. *Eur. J. Org. Chem.* **2014**, *2014*, 2668.

(11) Rodebaugh, R.; Debenham, J. S.; Fraser-Reid, B.; Snyder, J. P. *J. Org. Chem.* **1999**, *64*, 1758.

(12) (a) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328. (b) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(13) Kodomari, M.; Satoh, H.; Yoshitomi, S. *Nippon Kagaku Kaishi* **1986**, 1813.

(14) Shao, L.-X.; Shi, M. *Synlett* **2006**, 1269.

(15) Kabalka, G. W.; Yang, K. *Synth. Commun.* **1998**, *28*, 3807.