Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

New Application of N-Halosuccinimide/PPh_3 for the Halogenation of Propargyl Alcohols to Haloallenes

Xin Du [a], Yao Dai [a], Ren He [a], Shirong Lu [a] & Ming Bao [a]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China

Published online: 07 Oct 2009.

To cite this article: Xin Du, Yao Dai, Ren He, Shirong Lu & Ming Bao (2009) New Application of N-Halosuccinimide/PPh_3 for the Halogenation of Propargyl Alcohols to Haloallenes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:21, 3940-3949, DOI: 10.1080/00397910902883587

To link to this article: http://dx.doi.org/10.1080/00397910902883587

Synthetic Communications®, 39: 3940–3949, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910902883587

Taylor & Francis
Taylor & Francis Group

New Application of *N*-Halosuccinimide/PPh_3 for the Halogenation of Propargyl Alcohols to Haloallenes

Xin Du, Yao Dai, Ren He, Shirong Lu, and Ming Bao
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China

Abstract: An efficient and convenient new method has been developed for the preparation of haloallenes from propargyl alcohols by a reagent combination of *N*-halosuccinimide and triphenylphosphine. Chloroallenes **2** and bromoallenes **3** were obtained exclusively in moderate to good yields with regioselectivity.

Keywords: Haloallene, *N*-halosuccinimide, preparation, propargyl alcohol, triphenylphisphine

INTRODUCTION

Haloallenes can be used as synthetic intermediates in organic synthesis,[1–3] and the haloallene moieties have been found in many molecules of natural products.[4] Over the past few years, several synthetic methods, including the isomerization of 3-bromo- and 3-chloropropyne in the presence of cuprous halide;[5] the conversion of propargyl alcohols by halogenating reagents such as thionyl chloride,[6] $TiCl_4$/tertiary alkylamine,[7] and hydrochloric acid;[8] and the conversion of propargylic methanesulfonate by a halocuprate[9] have been reported for the purpose of preparing haloallenes. However, using these methods to synthesize haloallenes often has drawbacks: (i) poor yield, (ii) frequent obtaining

Received October 5, 2008.
Address correspondence to Ming Bao, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China. E-mail: mingbao@dlut.edu.cn

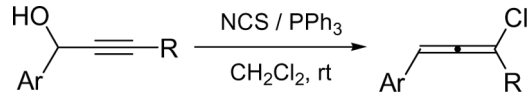
of a mixture, (iii) use of toxic halogenating reagent, and (iv) difficulty of operation. During the course of our research on the preparation of haloallene, we found that propargyl alcohols can be converted effectively to corresponding haloallenes by a reagent combination of *N*-halosuccinimide and triphenylphosphine under mild conditions. Herein, we report this efficient and convenient new method.

RESULTS AND DISCUSSION

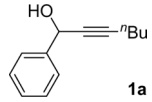
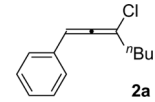
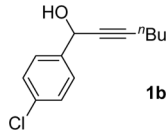
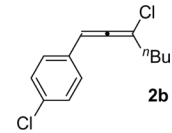
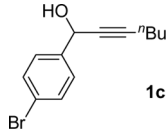
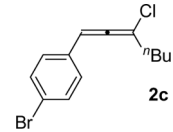
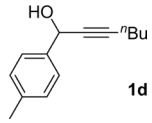
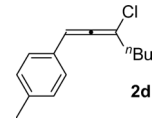
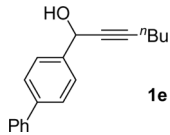
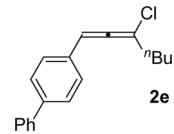
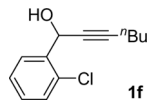
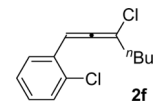
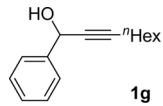
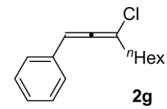
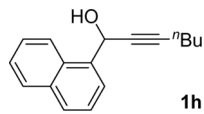
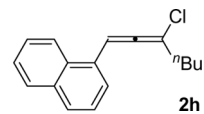
To the best of our knowledge, there is no report of the use of *N*-halosuccinimide as a halogenating reagent for the conversion of propargyl alcohols to haloallenes. It is easier to handle than other halogenating reagents, and it is also readily available. We first examined the reaction of 1-phenylhept-2-yn-1-ol (**1a**) with *N*-chlorosuccinimide (NCS) and triphenylphosphine in dichloromethane at room temperature to give the corresponding chloroallene (**2a**) in 83% yield (Table 1, entry 1). The success of the reaction encouraged us to perform reactions of various propargyl alcohols with NCS in the presence of triphenylphosphine, and the results are shown in Table 1. Neither the electron-donating group nor the electron-withdrawing group located at the *para* position of aromatic ring significantly influenced the chlorination, except for the phenyl group, and the yields of the chloroallenes **2b**–**d** were in the range of 80–88% (entries 2–4); a lesser yield was obtained from the reaction of *para* phenyl-substituted substrate (**1e**) (entry 5). In comparison with the *para* chlorine-substituted substrate (**1b**), a lesser reactivity of *ortho* chlorine-substituted substrate (**1f**) was found, which is perhaps due to the steric hindrance of *ortho*-chlorine atom (61%, entry 6). When the *n*-butyl group on **1a** was changed to *n*-hexyl group, the chlorination also proceeded smoothly to give the desired chloroallene (**2g**) in good yield (83%, entry 7). The naphthyl propargyl alcohols (**1h** and **1i**) were also employed to attempt this type of chlorination reaction but failed to obtain chloroallene (**2h** and **2i**) in satisfactory yields, even if the reaction time was prolonged (entries 8 and 9).

We then examined the bromination of propargyl alcohols **1b**–**d** and **1f** with *N*-bromosuccinimide (NBS) and triphenylphosphine, the results of which are summarized in Table 2. When the reaction of **1b** was performed under these conditions, the desired bromoallene **3b** was obtained in 86% yield (entry 1). Good yields of bromoallenes **3c** and **d** were obtained from the reactions of **1c** and **1d** (85% and 81%, respectively; entries 2 and 3). As with the previously described chlorination, the bromination of **1f** gave bromoallene **3f** in relatively lesser yield (62%, entry 4).

Table 1. Preparation of chloroallenes **2** from propargyl alcohols **1** using NCS/PPh_3[a]

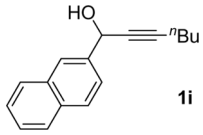
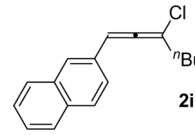


1 **2**

Entry	Substrate **1**	Time (h)	Product **2**	Yield (%)[b]
1	 **1a**	1	 **2a**	83
2	 **1b**	1	 **2b**	88
3	 **1c**	1	 **2c**	86
4	 **1d**	3	 **2d**	80
5	 **1e**	1	 **2e**	55
6	 **1f**	1	 **2f**	61
7	 **1g**	1	 **2g**	82
8	 **1h**	8	 **2h**	Trace

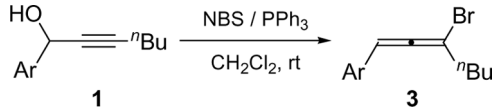
(*Continued*)

Table 1. Continued

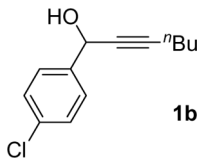
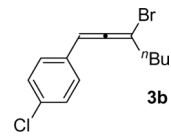
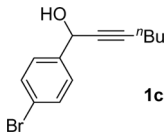
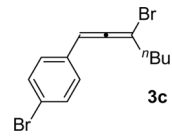
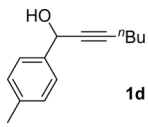
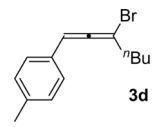
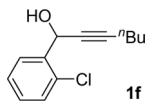
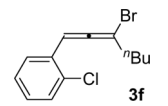
Entry	Substrate **1**	Time (h)	Product **2**	Yield (%)[b]
9	 **1i**	8	 **2i**	Trace

[a]All products are unknown compounds and were characterized by IR, ^{1}H and ^{13}C NMR, and HRMS.
[b]Isolated yields.

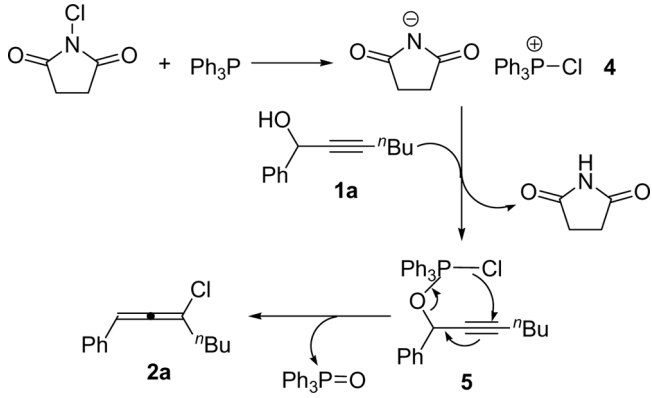
Table 2. Preparation of bromoallenes **3** from propargyl alcohols **1** using NBS/PPh_3[a]



1 **3**

Entry	Substrate **1**	Time (h)	Product **2**	Yield (%)[b]
1	 **1b**	1	 **3b**	86
2	 **1c**	1	 **3c**	85
3	 **1d**	1	 **3d**	81
4	 **1f**	3	 **3f**	62

[a]All products are unknown compounds and were characterized by IR, ^{1}H and ^{13}C NMR, and HRMS.
[b]Isolated yields.



Scheme 1. Proposed mechanism for the preparation of chloroallenes **2** from propargyl alcohols **1** using NCS/PPh_3.

The formation of haloallenes from propargyl alcohols is most likely to proceed through a halodeoxosubstitution and can be rationalized as follows (Scheme 1): NCS reacted with PPh_3 to produce phosphonium salt **4**,[10] which then reacted with propargyl alcohol **1a** to generate intermediate **5** and succinimide. Intermediate **5** underwent intramolecular halodeoxosubstitution to form chloroallene **2a** and generated triphenylphosphine oxide. The formation of succinimide and triphenylphosphine oxide in the halogenation of propargyl alcohols **1** was confirmed through isolation and NMR (^1H and ^{13}C or ^{31}P) determination of these by-products.

In summary, we have demonstrated an efficient and convenient method for the preparation of haloallenes. In this method, for the first time, the reagent combination of *N*-halosuccinimide and triphenylphosphine was utilized to convert propargyl alcohols to haloallenes. This type of formation of haloallenes from propargyl alcohols was achieved through intramolecular halodeoxosubstitution, and consequently the haloallenes were obtained exclusively with regioselectivity. An aryl substituent in the propargyl alcohol is essential for this reaction.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian Inova-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). The chemical shifts are reported in parts per million (ppm) downfield (δ) from tetramethylsilane (TMS). Infrared (IR) spectra were recorded on a Nexus Fourier transform (FT)–IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometer

(Micromass, England) equipped with Z-spray ionization source. Thin-layer chromatography (TLC) was carried out on SiO_2 (silica gel 60 F_{254}, Merck). Flash chromatography was carried out on SiO_2 (silica gel 60, 200–300 meth). Aldehydes, 1-hexyne, and 1-octyne were all commercial products and were used without further purification.

General Procedure for the Preparation of Propargyl Alcohols

A mixture of metal sodium (2.30 g, 10.0 mmol) and alkyne (10.0 mmol) in 40 mL of diethyl ether was stirred at room temperature under a nitrogen atmosphere until the sodium was completely consumed. Then the mixture was cooled to $-10°C$, and a solution of aldehyde (5.0 mmol) in 20 mL of diethyl ether was added dropwise slowly through a dropping funnel at the same temperature. After the reaction mixture was stirred at $-10°C$ for 2–5 h, dilute hydrochloric acid (0.5 M, 10 mL) was added to quench the reaction. The product was extracted with diethyl ether (3×15 mL), and the combined organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica-gel column chromatography (eluent: petroleum ether (60–90°C)–ethyl acetate = 10:1) to afford pure propargyl alcohols in 50–70% yields.

General Procedure for the Preparation of Haloallenes

A mixture of propargyl alcohol (1.00 mmol), *N*-halosuccinimide (1.55 mmol), and triphenylphosphine (1.50 mmol) in 10 mL of dichloromethane was stirred magnetically at room temperature for 1–3 h. The solvent was removed under reduced pressure, and then the crude product was purified by flash-column chromatography on silica gel (eluent: hexane) to give pure haloallenes in 55–88% yields (Tables 1 and 2).

Spectral Data for New Compounds

1-Biphenyl-4-ylhept-2-yn-1-ol (**1e**)

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.62 (m, 6H), 7.43–7.47 (m, 2H), 7.36–7.38 (m, 1H), 5.51 (m, 1H), 2.31 (dt, $J = 2.0$, 6.8 Hz, 2H), 2.14 (bs, 1H), 1.52–1.58 (m, 2H), 1.42–1.48 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.7, 140.3, 128.8, 128.8, 127.4, 127.3, 127.3, 127.1, 127.1, 127.0, 127.0, 87.8, 79.9, 64.6, 30.7,

22.0, 18.5, 13.6; IR (neat) ν: 3334, 2956, 2933, 2859, 2222, 1487, 1465, 1405, 1028, 1014, 1006, 988, 857, 757, 738, 693 cm^{-1}; HRMS (EI) calcd. for $C_{19}H_{20}O$: 264.1514 $[M]^+$; found: 264.1517.

Naphthalen-1-ylhept-2-yn-1-ol (**1i**)

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 1H), 7.79–7.83 (m, 3H), 7.63 (dd, $J = 1.6$, 8.4 Hz, 1H), 7.44–7.47 (m, 2H), 5.57 (s, 1H), 2.48 (bs, 1H), 2.26–2.30 (m, 2H), 1.47–1.50 (m, 2H), 1.38–1.42 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 133.2, 133.1, 128.4, 128.2, 127.6, 126.2, 126.1, 125.3, 124.7, 87.9, 80.0, 64.9, 30.6, 22.0, 18.5, 13.6.

(3-Chlorohepta-1,2-dienyl)-benzene (**2a**)

Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.35 (m, 4H), 7.26–7.27 (m, 1H), 6.42 (t, $J = 2.8$ Hz, 1H), 2.44–2.50 (m, 2H), 1.53–1.59 (m, 2H), 1.37–1.42 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 133.5, 128.9, 128.9, 128.3, 127.9, 127.9, 109.0, 101.9, 36.5, 29.9, 22.0, 14.0; IR (neat) ν: 3064, 3033, 2960, 2933, 2873, 1955, 1453, 1265, 1176, 697 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{15}Cl$: 206.0862 $[M]^+$; found: 206.0871.

1-Chloro-4-(3-chlorohepta-1,2-dienyl)-benzene (**2b**)

Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.38 (t, $J = 2.8$ Hz, 1H), 2.44–2.48 (m, 2H), 1.54–1.57 (m, 2H), 1.38–1.41 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 133.9, 131.9, 129.0, 129.0, 128.9, 128.9, 109.2, 100.6, 36.2, 29.2, 21.8, 13.8; IR (neat) ν: 2958, 2930, 2872, 1955, 1491, 1091, 1014, 852, 506 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}Cl_2$: 240.0473 $[M]^+$; found: 240.0484.

1-Bromo-4-(3-chlorohepta-1,2-dienyl)-benzene (**2c**)

Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.36 (t, $J = 2.8$ Hz, 1H), 2.44–2.46 (m, 2H), 1.54–1.57 (m, 2H), 1.35–1.45 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 132.3, 131.9, 131.9, 131.4, 129.2, 129.2, 109.3, 100.7, 36.2, 29.2, 21.9, 13.8; IR(neat) ν: 2957, 2927, 2858, 1955, 1487, 1464, 1379, 1071, 1011, 851 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}ClBr$: 283.9967 $[M]^+$; found: 283.9974.

1-(3-Chlorohepta-1,2-dienyl)-4-methyl-benzene (**2d**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, $J = 8$ Hz, 2H), 7.14 (d, $J = 8$ Hz, 2H), 6.40 (bs, 1H), 2.43–2.47 (m, 2H), 2.35 (s, 3H), 1.52–1.60 (m, 2H), 1.36–1.42 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 138.2, 130.4, 129.5, 129.5, 127.7, 127.7, 108.6, 101.7, 36.4, 29.3, 21.9, 21.2, 13.8; IR (neat) ν: 2959, 2929, 2872, 1957, 1606, 1513, 1457, 812, 751 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{17}Cl$:220.1019 $[M]^+$; found: 220.1015.

4-(3-Chlorohepta-1,2-dienyl)-biphenyl (**2e**)

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.59 (m, 4H), 7.39–7.45 (m, 4H), 7.32–7.36 (m, 1H), 6.46 (bs, 1H), 2.46–2.50 (m, 2H), 1.55–1.62 (m, 2H), 1.38–1.45 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 141.0, 140.5, 132.3, 128.8, 128.8, 128.2, 128.2, 127.5, 127.5, 127.5, 127.0, 127.0, 108.9, 101.4, 36.4, 29.3, 21.9, 13.8; IR (neat) ν: 3433, 2955, 2931, 2870, 1951, 1487, 1465, 1456, 1378, 1328, 1107, 1007, 939, 866, 762, 723, 708, 695 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{19}Cl$: 282.1175$[M]^+$; found: 282.1185.

1-Chloro-2-(3-chlorohepta-1,2-dienyl)-benzene (**2f**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.36 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.16–7.26 (m, 2H), 6.87 (t, $J = 3.2$ Hz, 1H), 2.44–2.49 (m, 2H), 1.53–1.61 (m, 2H), 1.34–1.44 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 133.1, 131.1, 129.9, 129.1, 129.1, 127.0, 109.3, 97.9, 36.2, 29.2, 21.9, 13.8; IR(neat) ν: 2958, 2930, 2872, 1957, 1477, 1444, 1050, 1032, 834, 751 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}Cl_2$: 240.0473 $[M]^+$; found: 240.0471.

(3-Chlorononа-1,2-dienyl)-benzene (**2g**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.34 (m, 4H), 7.26–7.27 (m, 1H), 6.42 (t, $J = 2.8$ Hz, 1H), 2.43–2.46 (m, 2H), 1.53–1.58 (m, 2H), 1.25–1.29 (m, 6H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 133.3, 128.7, 128.7, 128.2, 127.8, 127.8, 109.0, 101.7, 36.6, 31.5, 28.4, 27.1, 22.6, 14.0; IR (neat) ν: 2955, 2928, 2857, 1954, 1496, 1459, 746, 651 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{19}Cl$: 234.1175$[M]^+$; found: 234.1180.

1-(3-Bromohepta-1,2-dienyl)-4-chloro-benzene (**3b**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.33 (m, 2H), 7.22–7.26 (m, 2H), 6.14 (t, $J = 2.8$ Hz, 1H), 2.50–2.55 (m, 2H), 1.50–1.59 (m, 2H), 1.34–1.41 (m, 2H), 0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 133.9, 131.6, 129.0, 129.0, 128.9, 128.9, 99.3, 96.4, 37.7, 29.7, 21.8, 13.8; IR (neat) ν: 2924, 2853, 1952, 1491, 1464, 1378, 1093, 1014, 850 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}ClBr$: 283.9967 $[M - Br]^+$; found: 205.0786.

1-Bromo-4-(3-bromohepta-1,2-dienyl)-benzene (**3c**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.13 (t, $J = 2.8$ Hz, 1H), 2.50–2.54 (m, 2H), 1.51–1.59 (m, 2H), 1.35–1.42 (m, 2H), 0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 132.0, 131.9, 131.9, 129.2, 129.2, 122.1, 99.4, 96.4, 37.7, 31.6, 22.7, 14.1; IR (neat) ν: 2957, 2929, 2871, 1952, 1587, 1487, 1464, 1379, 1109, 1071, 1010, 953, 850, 818 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}Br_2$: 327.9462 $[M]^+$; found: 327.9466.

1-(3-Bromohepta-1,2-dienyl)-4-methyl-benzene (**3d**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, $J = 8$ Hz, 2H), 7.14 (d, $J = 8$ Hz, 2H), 6.18 (t, $J = 2.8$ Hz, 1H), 2.50–2.54 (m, 2H), 2.35 (s, 3H), 1.52–1.60 (m, 2H), 1.36–1.43 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 138.2, 130.1, 129.5, 129.5, 127.7, 127.7, 100.4, 98.9, 37.9, 30.1, 21.9, 21.3, 13.8; IR (neat) ν: 2957, 2929, 2860, 1952, 1514, 1458, 1176, 1108, 849, 800, 752 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{17}Br$: 264.0514 $[M - Br]^+$; found: 185.1332.

1-(3-Bromohepta-1,2-dienyl)-2-chloro-benzene (**3f**)

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, $J = 1.6$, 8.0 Hz, 1H), 7.35 (dd, $J = 1.6$, 8.0 Hz, 1H), 7.22–7.26 (m, 1H), 7.15–7.19 (m, 1H), 6.65 (t, $J = 2.8$ Hz, 1H), 2.51–2.55 (m, 2H), 1.53–1.60 (m, 2H), 1.34–1.43 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 133.1, 130.8, 129.9, 129.9, 129.1, 127.0, 96.5, 96.4, 37.6, 30.0, 21.8, 13.7; IR (neat) ν: 2957, 2928, 2860, 1953, 1477, 1465, 1444, 1380, 1050, 831, 751 cm^{-1}; HRMS (EI) calcd. for $C_{13}H_{14}ClBr$: 283.9967 $[M - Br]^+$; found: 205.0798.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (20572010) for financial support. This work was partly supported by the Program for Changjiang Scholars and Innovative Research Teams in Universities (IRT0711).

REFERENCES

1. Sromek, A. W.; Rubina, M.; Gevorgyan, V. 1,2-Halogen migration in haloallenyl ketones: Regiodivergent synthesis of halofurans. *J. Am. Chem. Soc.* **2005**, *127*, 10500–10501.
2. Corey, E. J.; Kang, J. Stereospecific total synthesis of 11(R)-HETE (2), lipoxygenation product of arachidonic acid via the rostaglandin pathway. *J. Am. Chem. Soc.* **1981**, *103*, 4618–4619.
3. Taylor, D. R. The chemistry of allenes. *Chem. Rev.* **1967**, *67*, 317–359.
4. Hoffmann-Roder, A.; Krause, N. Synthesis and properties of allenic natural products and pharmaceuticals. *Angew. Chem. Int. Ed.* **2004**, *43*, 1196–1216.
5. Jacobs, T. L.; Brill, W. F. Haloallenes. *J. Am. Chem. Soc.* **1953**, *75*, 1314–1317.
6. (a) Jacobs, T. L.; Petty, W. L.; Teach, E. G. The reaction of propargyl alcohols with thionyl chloridel. *J. Am. Chem. Soc.* **1960**, *82*, 4094–4097; (b) Hennion, G. F.; Lynch Jr., C. A. Chlorides derived from 1-ethynylcyclohexanol. *J. Org. Chem.* **1960**, *25*, 1330–1333; (c) Jacobs, T. L.; Fenton, D. M. Aryl-substituted propargyl alcohols and related compounds. *J. Org. Chem.* **1965**, *30*, 1808–1812; (d) Jacobs, T. L.; Hall, C.; Babbe, D. A.; Prempree, P. Aryl-substituted propargyl alcohols and related compounds: 11.l-Mesityll,3-diphenyl-2-propyn-1-ol and l-(α-naphthyl)-1,3-diphenyl-2-propyn-l-ol. *J. Org. Chem.* **1967**, *32*, 2283–2286.
7. Karunakar, G. V.; Periasamy, M. Conversion of propargyl alcohols to chloroallenes and arylalkynes using the $TiCl_4/R_3N$ reagent system. *J. Org. Chem.* **2006**, *71*, 7463–7466.
8. Hennion, G. F.; Sheehan, J. J.; Maloney, D. E. The reaction of dimethylethynyl carbinol with hydrochloric acid. *J. Am. Chem. Soc.* **1950**, *72*, 3542–3545.
9. Elsevier, C. J.; Meijer, J.; Tadema, G.; Stehouwer, P. M.; Bos, H. J. T.; Vermeer, P. A highly stereoselective synthesis of allenic halides by means of halocuprate-induced substitution in propargylic methanesulfonates. *J. Org. Chem.* **1982**, *47*, 2194–2196.
10. (a) Sugimoto, O.; Mori, M.; Moriya, K.; Tanji, K. Application of phosphonium salts to the reactions of various kinds of amides. *Helv. Chim. Acta* **2001**, *84*, 1112–1118; (b) Tanji, K.; Koshio, J.; Sugimoto, O. Microwave-assisted dehydration and chlorination using phosphonium salt. *Synth. Commun.* **2005**, *35*, 1983–1987.