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Studies on Electrophilic Reaction of Tertiary 2,3-Allenols with NBS in H_2O or Aqueous MeCN: An Efficient Selective Synthesis of 2-Bromoallylic Ketones, 1,2-Allenyl Ketones, or 3-Bromo-2,5-dihydrofurans

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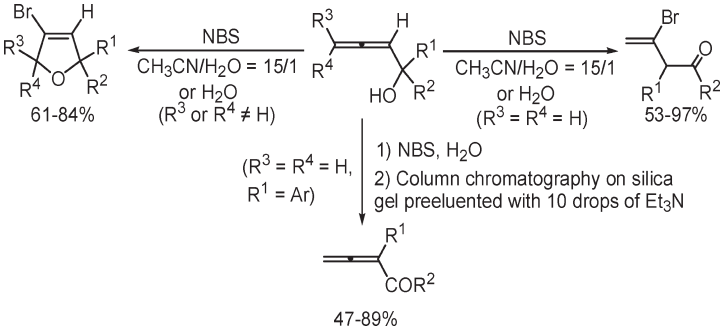
Received August 31, 2009



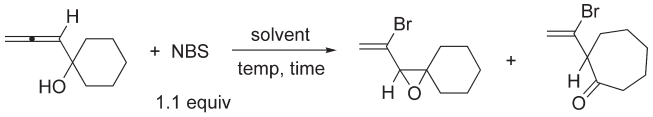
Previously, we observed that the electrophilic reaction of 2,3-allenols with X^+ (X = Br, I) affords 3-halo-2-alkenals or 2-halo-2-alkenyl ketones in aqueous MeCN (MeCN/H_2O = 15:1). However, the reaction of tertiary 2,3-allenols with NBS under these reaction conditions affords a mixture of rearrangement products (aldehydes or ketones) together with 1-bromovinyl epoxides in a low selectivity. Due to the synthetic potential of 2-haloallylic ketones, we decided to explore this reaction further. After screening, we observed that the electrophilic reaction of terminal tertiary 2,3-allenols with NBS in water affords 2-bromoallylic ketones highly selectively in up to 97% yields via a sequential electrophilic interaction of Br^+ with the allene moiety to form a possible three-membered bromonium intermediate with the more substituted C═C bond, which would be followed by 1,2-aryl or 1,2-alkyl shift to open the strained three-membered ring and proton elimination to form the carbonyl functionality. When both R^1 and R^2 (the substituents on the carbon atom connected to the hydroxyl groups) are alkyl groups, one of these two groups is migrated; with 1,2-propadienyl cycloalkanols, a ring expansion reaction was observed; with R^1 being an aryl group, R^1 would be transferred exclusively to form the 2-bromoallylic ketones. Interestingly, these 2-bromo-1-aryl-2-propenyl ketones may easily be converted into 1,2-allenyl ketones after column chromatography on silica gel pre-eluented with 10 drops of Et_3N; when there is at least an alkyl substituent on the 4-position of the tertiary 2,3-allenols, their electrophilic reaction with NBS in CH_3CN/H_2O = 15/1 or H_2O, under the same reaction conditions as above, affords 3-bromo-2,5-dihydrofurans in 61−84% yields, indicating that the electronic effect and the steric effect of the two C═C bonds determine the reaction pathway, i.e., the Br^+ interacts with the C═C bond at the 3-position.

Introduction

Electrophilic addition reactions of allenes have been becoming more and more useful in organic synthesis since two functionalities may be introduced within one synthetic operation.[1,2] In 2005, we reported that the electrophilic reaction of 2,3-allenols with X^+ affords 3-halo-3-alkenals or 2-halo-2-alkenyl ketones in 37% to 93% yields with good

DOI: 10.1021/jo9018717 Published on Web 10/29/2009

TABLE 1. Electrophilic Reaction of 1-(Propadienyl)cyclohexanol 1a with NBS[a]



1a **2a** **3a**

entry	solvent	*T* (°C)	*t* (h)	yield of **2a** (%)	yield of **3a** (%)	recovery of **1a** (%)
1	$MeCN/H_2O$ = 15/1	rt	1	50	19	0
2	$MeCN/H_2O$ = 15/1	0	2	54	25	0
3	THF	rt	3	29	13	6
4	MeCN	rt	10	22	21	33
5	$MeNO_2$	rt	2	6	17	29
6	CH_2Cl_2	rt	3	5	4	62
7	CCl_4	rt	3	0	0	60
8	MeOH	rt	2	complicated		
9	1,4-dioxane	rt	2	10	7	52
10	$MeCN/H_2O$ = 5/1	rt	10	50	34	0
11	$MeCN/H_2O$ = 1/1	rt	10	26	48	0
12	$MeCN/H_2O$ = 1/10	rt	2	12	55	0
13	H_2O	rt	2	10	58	0
14[b]	H_2O	rt	2	8	60 (58)	0
15[c]	H_2O	rt	2	7	51	0
16[d]	H_2O	rt	2	7	50	0
17[e]	H_2O	rt	2	4	20	0
18[b]	H_2O	60	2	6	51	0
19[b]	H_2O	80	2	8	49	0

[a]NMR yields determined by using CH_2Br_2 as the internal standard. The isolated yield is given in parentheses. [b]1.0 equiv of NBS was used. [c]1.2 equiv of NBS were used. [d]1.5 equiv of NBS were used. [e]2.0 equiv of NBS were used.

regioselectivity in aqueous MeCN ($MeCN/H_2O$ = 15/1), in which a C−C bond was cleaved due to the rearrangement of a cationic intermediate.[3] However, when we tried to extend this chemistry to tertiary 2,3-allenols, it was observed that the formation of the epoxide is a major side reaction. In 2008, Okamoto et al. reported the reaction of 2-substituted tertiary 2,3-allenols with NBS, affording cyclic 2-haloallylic ketones in $MeCN/H_2O$ = 15/1 in moderate yields (38−79%) with the formation of epoxide being reported only in one case.[4] In this paper, we wish to report our detailed study on the electrophilic reaction of tertiary 2,3-allenols with NBS, especially the solvent effect on the selectivity of carbonyl products vs. epoxides as well as the electronic and steric effects on the regioselectivity of the reaction of Br^+ with the different C=C bonds of the allene moiety.

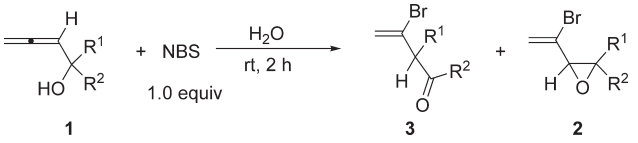
Results and Discussion

Electrophilic Reaction of Tertiary 2,3-Allenols. First, we used 1-(propadienyl)cyclohexanol **1a** as the model substrate. The reaction in $MeCN/H_2O$ = 15/1[3] afforded a mixture of 2-bromovinyl-substituted epoxide **2a**[5] and the ring-expanded 2-bromovinyl seven-membered cyclic ketone **3a** in 69% combined yield with a selectivity of 2.6:1 (Table 1, entry 1). It should be noted that the reaction afforded **2a** and **3a** in essentially the same ratio even after 4 h. Furthermore, treatment of pure epoxide **2a** under the conditions listed in entry 1 for 12 h did not yield any **3a**. These two facts indicate that epoxide **2a** is not the kinetic product and did not serve as an intermediate for the formation of ketone **3a**. To increase the selectivity of ketone/epoxide, screening of different reaction conditions was conducted: the reaction at 0 °C led to a slight increase of the yield (Table 1, entry 2). Then we screened the most commonly used solvents, such as THF, MeCN, $MeNO_2$, CH_2Cl_2, CCl_4, MeOH, and 1,4-dioxane; however, all the results were poor with **1a** being recovered to some extent (Table 1, entries 3−9). The effect of the ratio of the mixed solvent $MeCN/H_2O$ on the reaction was also screened (Table 1, entries 10−12). To our surprise, the reaction in pure water afforded the α-(2-bromoallyl)cycloheptanone **3a** in 58% yield together with epoxide **2a** in 10% yield (Table 1, entry 13). Best results were achieved by running the reaction in water, using 1.0 equiv of NBS to afford **3a** in 60% yield (58% isolated yield) and epoxide **2a** in 8% yield (Table 1, entry 14). Increasing the amount of NBS led to reduced yields (Table 1, entries 15−17). The reaction at a higher temperature afforded the products in slightly lower yields (Table 1, entries 18 and 19). Thus, the reaction conditions presented in entry 14 of Table 1 were defined as the standard conditions for further study.

The electrophilic reaction of tertiary 2,3-allenols **1** with different types of R^1 and R^2 at the 1-position with NBS was then studied by applying the standard reaction conditions: The reaction of cyclic 2,3-allenols **1b−d** with NBS afforded ring-expanded products α-(1-bromovinyl)cycloketones **3b−d** in moderate yields via a 1,2-alkyl shift process (Table 2, entries 1−4). The reaction of 1-(propadienyl)cyclopentanol **1b** in H_2O afforded the corresponding rearrangement product **3b** in moderate NMR yield (59%) together with another unidentified product (Table 2, entry 1), while the reaction in $MeCN/H_2O$ = 15/1 afforded the compound **3b** as the only product (Table 2, entry 2). It is interesting to

(1) For a review, see: Ma, S. Ionic Addition to Allenes. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004.
(2) (a) Ma, S. *Pure Appl. Chem.* **2007**, *79*, 261. (b) Ma, S. *Acc. Chem. Res.* DOI: 10.1021/ar900153r. Published Online: July 15, 2009.
(3) (a) Fu, C.; Li, J.; Ma, S. *Chem. Commun.* **2005**, 4119. (b) Li, J.; Fu, C.; Chen, G.; Chai, G.; Ma, S. *Adv. Synth. Catal.* **2008**, *350*, 1376.
(4) He, J.; Shibata, D.; Ohno, C.; Okamoto, S. *Tetrahedron Lett.* **2008**, *49*, 6724.
(5) Friesen, R. W.; Blouin, M. *J. Org. Chem.* **1993**, *58*, 1653.

TABLE 2. Electrophilic Reaction of Tertiary 2,3-Allenols 1 with NBS in Water



1 3 2

entry	R^1	R^2	isolated yield of **3** (%)	NMR yield of **2** (%)
1	$(CH_2)_4$ (**1b**)		−[a] (**3b**)	0
2[b]	$(CH_2)_4$ (**1b**)		53 (**3b**)	0
3	$(CH_2)_6$ (**1c**)		62 (**3c**)	12
4	$(CH_2)_7$ (**1d**)		58 (**3d**)	8
5	*n*-C_3H_7	*n*-C_3H_7 (**1e**)	60 (**3e**)	4
6	*n*-C_4H_9	*n*-C_4H_9 (**1f**)	60 (**3f**)	4
7	Ph	CH_3 (**1g**)	97 (**3g**)	0
8	Ph	C_2H_5 (**1h**)	93 (**3h**)	0
9	*m*-$CH_3C_6H_4$	CH_3 (**1i**)	82 (**3i**)	0
10	*p*-$CH_3C_6H_4$	CH_3 (**1j**)	79 (**3j**)	0
11	Ph	Ph (**1k**)	79 (**3k**)	0

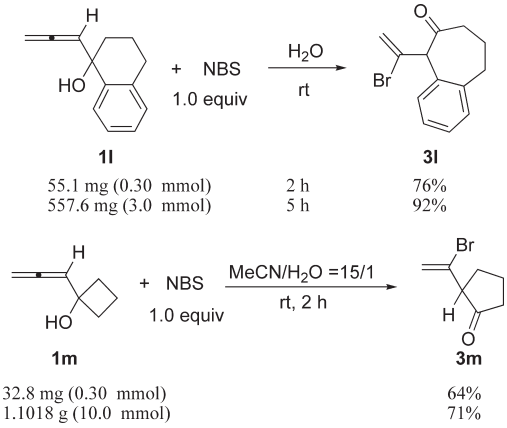
[a]59% NMR yield together with another unidentified product. [b]MeCN/H_2O = 15/1 was used as solvent.

observe that even the not readily available eight- or nine-membered rings[6] may be formed easily (Table 2, entries 3 and 4). The yields of epoxides **2c**,**d** were at the level of 8−12% for **1c**,**d** (Table 2, entries 3 and 4) while the formation of epoxide **2b** was not observed in the reaction of **1b** (Table 2, entry 2). Furthermore, we were happy to see that even the reaction of the substrates with R^1 and R^2 being separate alkyl groups, i.e., **1e** and **1f**, afforded 1,2-alkyl shift products **3e** and **3f** in moderate yields with 4% of epoxide products **2e** and **2f** (Table 2, entries 5 and 6). The Br^+-induced 1,2-shift reaction of the 2,3-allenols **1** with R^1 being an aryl group showed very good selectivity, but only the 1,2-aryl (R^1) shift products **3** were formed in good to excellent yields (79−97%) (Table 2, entries 7−11). The reaction of the substrate **1k** with R^1 and R^2 both being phenyl also afforded the 1,2-aryl shift product **3k** in 79% yield (Table 2, entry 11).

The reaction may also be extended to 1-(propadienyl)-1,2,3,4-tetrahydronaphth-1-ol ***1l***, affording the 1,2-aryl shift product 5-(1′-bromovinyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]-annulen-6-one ***3l*** in only 76% yield in 2 h with a 0.3 mmol scale reaction; when 3.0 mmol of ***1l*** was used, ***3l*** was afforded in a much higher yield (92%) in 5 h with the complete consumption of the starting material. The structure of the product ***3l*** was further confirmed by its X-ray diffraction study (Figure 1 in the Supporting Information).[7] The reaction of 1-(propadienyl)cyclobutanol **1m** also afforded 2-(1′-bromovinyl)cyclopentanone **3m** in a higher yield (71%) when 10.0 mmol of **1m** was used as compared to a 0.3 mmol scale reaction (64%) (Scheme 1).

One-Pot Synthesis of 1-Aryl-1,2-allenyl Ketones. It is interesting for us to observe that 1-aryl-2-halo-2-propenyl ketones may be partially converted to 1-aryl-1,2-propadienyl ketones[8] upon purification via chromatography on silica gel. Further study led us to note that 1-aryl-1,2-propadienyl ketones **3g**−**k** and **3n** may be converted to 1,2-allenyl ketones **4g**−**k** and **4n** in moderate to good yields cleanly and exclusively upon column chromatography on silica gel pre-eluented with 10 drops of Et_3N. Both 1-aryl-1,2-propdienyl aryl and alkyl ketones may be prepared (Table 3). The structure of the product **4i** was further confirmed by its X-ray diffraction study (Figure 2 in the Supporting Information).[9] When tertiary 2,3-allenol ***1l*** was treated with NBS followed by column chromatography on silica gel pre-eluented with 10 drops of Et_3N, 1,2-allenyl ketone ***4l*** was

SCHEME 1



(6) For a review of limitations in the synthesis of medium-sized ring carbocycles, see: Majhi, T. P.; Achari, B.; Chattopadhyay, P. *Heterocycles* **2007**, *71*, 1011.

(7) Crystal data for ***3l***: $C_{13}H_{13}OBr$, MW = 265.14, monoclinic, space group *P*2(1)/*n*, final *R* indices [$I > 2\sigma(I)$], $R_1 = 0.0204$, $wR_2 = 0.0516$, *R* indices (all data) $R_1 = 0.0216$, $wR_2 = 0.0524$, $a = 12.7860(4)$ Å, $b = 6.0794(2)$ Å, $c = 14.2698(4)$ Å, $\alpha = 90°$, $\beta = 99.934(2)°$, $\gamma = 90°$, $V = 1092.58(6)$ Å^3, $T = 173(2)$ K, $Z = 4$, reflections collected/unique 9937/1922 ($R_{int} = 0.0389$), number of observations [$> 2\sigma(I)$] 1831, parameters 145. File CCDC 713084 can be obtained free of charge from the CCDC via www.ccdc.cam.ak/conts/retrieving.html.

(8) (a) For a report on the formation of 1,2-propadienyl methyl ketone via the elimination of HBr from the *Z*/*E* mixture of 3-bromobut-3-en-2-one, see: Buono, G. *Synthesis* **1981**, 872. (b) For the formation of *N*-phenyl-2,3-butadienamide from the elimination of *N*-phenyl-3-bromo-3-butenamide, see: Zhao, Q.; Li, C. *Org. Lett.* **2008**, *10*, 4037.

(9) Crystal data of ***4i***: $C_{12}H_{12}O$, MW = 172.22, monoclinic, space group *P*2(1)/*n*, final *R* indices [$I > 2\sigma(I)$], $R_1 = 0.0373$, $wR_2 = 0.0997$, *R* indices (all data) $R_1 = 0.0411$, $wR_2 = 0.1044$, $a = 7.5594(3)$ Å, $b = 13.6697(5)$ Å, $c = 9.4364(3)$ Å, $\alpha = 90°$, $\beta = 93.7300(10)°$, $\gamma = 90°$, $V = 973.04(6)$ Å^3, $T = 173(2)$ K, $Z = 4$, reflections collected/unique 11007/1704 ($R_{int} = 0.0170$), number of observations [$> 2\sigma(I)$] 1535, parameters 126. File CCDC 736404 can be obtained free of charge from the CCDC via www.ccdc.cam.ak/conts/retrieving.html.

SCHEME 2

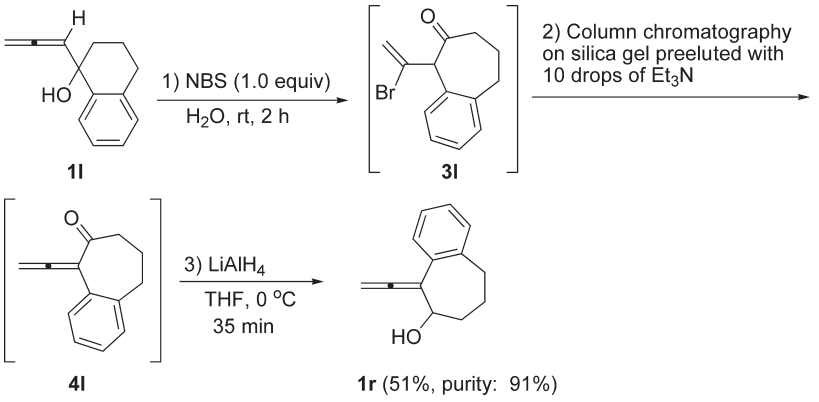
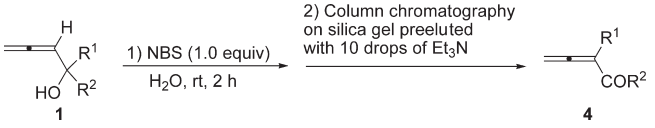
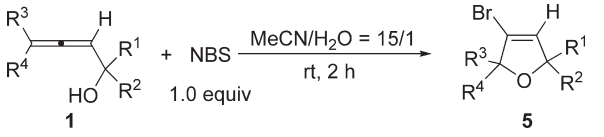


TABLE 3. Synthesis of 1-Aryl-1,2-allenyl Ketones 4 from Tertiary 2,3-Allenols 1g-n



entry	R^1	R^2	isolated yield (%)
1	Ph	CH_3 (**1g**)	74 (**4g**)
2	Ph	C_2H_5 (**1h**)	77 (**4h**)
3	*m*-$CH_3C_6H_4$	CH_3 (**1i**)	88 (**4i**)
4	*p*-$CH_3C_6H_4$	CH_3 (**1j**)	89 (**4j**)
5	Ph	Ph (**1k**)	74 (**4k**)
6	*p*-$NO_2C_6H_4$	CH_3 (**1n**)	47 (**4n**)

TABLE 4. Electrophilic Cyclization of 4-Substituted Tertiary 2,3-Allenols 1o-g with NBS



entry	R^1	R^2	R^3	R^4	isolated yield (%)
1	$(CH_2)_4$		Me	Me (**1o**)	71 (**5o**)
2[a]	$(CH_2)_4$		Me	Me (**1o**)	67 (**5o**)
3	Ph	Me	Me	Me (**1p**)	84 (**5p**)
4[a]	Ph	Me	Me	Me (**1p**)	69 (**5p**)
5	$(CH_2)_4$		*n*-C_5H_{11}	H (**1q**)	73 (**5q**)
6[a,b]	$(CH_2)_4$		*n*-C_5H_{11}	H (**1q**)	61 (**5q**)

[a]With H_2O as solvent. [b]1.2 equiv of NBS were used.

formed via the intermediacy of ***3l*** (Scheme 1). However, this allenyl ketone is unstable, thus it was further reduced with $LiAlH_4$ to form cyclic 2,3-allenol **1r** in 51% combined yield for the three-step procedure (Scheme 2).

Synthesis of 3-Bromo-2,5-dihydrofurans from Substituted Tertiary 2,3-Allenols. However, this reaction could not be extended to substrates with substituent(s) at the 4-position of the starting 2,3-allenols: the reaction of 4-substituted tertiary 2,3-allenols **1o**−**q** with NBS failed to afford either **3**-type ketones or **2**-type epoxides. Instead, 3-bromo-2,5-dihydrofurans **5o**−**q** were formed as the only product in high yields either in H_2O (entries 2, 4, and 6, Table 4) or in MeCN:H_2O (15:1) (entries 1, 3, and 5, Table 4), indicating that Br^+ interacts with the C=C bond at the 3-position of 2,3-allenols exclusively (Table 4), which has been observed by Marshall et al.[10,11]

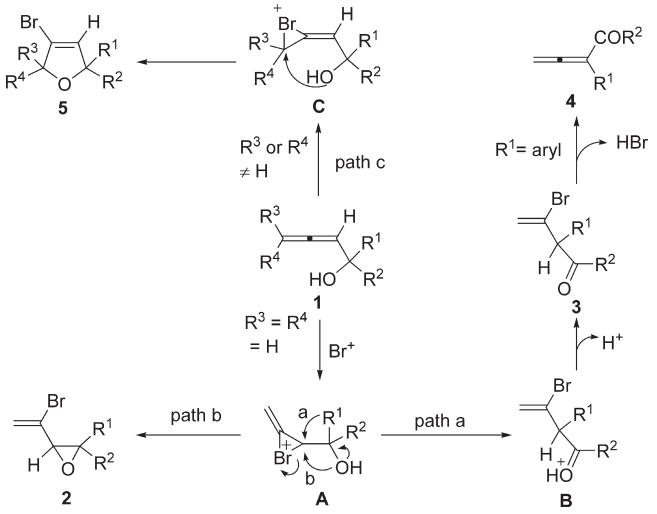
Mechanistic Discussion. On the basis of these observations, it is concluded that the regioselectivity for the C=C bond in the allene interacting with Br^+ depends largely on the electronic and steric effects of these two C=C bonds:[3] When $R^3 = R^4 = H$, the interaction of "X^+" with the relatively electron-rich internal C=C bond of the allene moiety would form the positively charged three-membered bromonium **A**, which undergoes a 1,2-shift of the aryl or alkyl group[12] to open the strained three-membered ring forming the cationic homoallylic alcohol intermediate **B**. Upon release of H^+ the reaction would form 2-bromoallylic ketones **3**, which can easily be converted to 1,2-allenyl ketones **4** via elimination of HBr due to the presence of the electron-withdrawing carbonyl group and the aryl group in **3** (path a).[9] When R^1 and R^2 are both alkyl groups, the 1,2-alkyl shift may be slower, and the competitive reaction occurs to form the epoxide product **2** as a byproduct via the intramolecular attack of the hydroxyl oxygen atom (path b). When R^3 or $R^4 \neq H$, the C=C bond at the 3-position of 2,3-allenols becomes more electron rich and less sterically hindered (as compared to the C=C bond at the 2-position) for 4-monosubstituted ones and very electron rich for 4,4-disubstituted ones, thus its reaction with "X^+" would favorably form positively charged three-membered bromonium **C**, which would be attacked by the intramolecular hydroxyl group affording 3-bromo-2,5-dihydrofuran **5** as the only product (Scheme 3, path c).[10] Regarding the effect of H_2O, it may stabilize the allenyl bromonium species and its hydrogen bonding with the hydroxyl group may slow down the epoxide formation, while allowing the slower aryl/alkyl Meerwein−Wagner 1,2-shift to compete.

(10) (a) Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1990**, *55*, 2995. (b) Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1991**, *56*, 4913.

(11) For recent reports on Ag^+ or Au^+-catalyzed cycloisomerization reactions of 2,3-allenols, see: (a) Mitasev, B.; Brummond, K. M. *Synlett* **2006**, 3100. (b) Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387. (c) Wei, L.-L.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773.

(12) (a) Nakamura, K.; Osamura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9112. (b) Hu, X.; Fan, C.; Zhang, F.; Tu, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 1702.

SCHEME 3. Proposed Mechanism for the Formation of Allylic Ketones 3, Epoxides 2, and 3-Bromo-2,5-dihydrofurans 5



Conclusion

In summary, it is concluded that the regioselectivity referring to which C=C bond of the allene moiety in tertiary 2,3-allenols would interact with NBS depends on the steric and electronic effects: with terminal tertiary 2,3-allenols, the relatively electron-rich C=C bond at the 2-position would react with NBS to form either 2-bromo-2-propenyl ketones or 1-bromovinyl epoxides via 1,2-shift/H^+-elimination or intramolecular attack of the hydroxyl group, respectively. The formation of epoxides may be reduced dramatically by conducting the reaction in water. With 4-substituted tertiary allenols, the substituent(s) at the 4-position increases the electron richness of the C=C bond at the 3-position, thus it reacts exclusively with NBS followed by intramolecular attack of the hydroxyl group to form 3-bromo-2,5-dihydrofurans. This electrophilic interaction of tertiary 2,3-allenols with NBS is useful for the selective synthesis of 2-bromoallylic ketones, 1,2-allenyl ketones, or 3-bromo-2,5-dihydrofurans. Due to the synthetic potential of these products, this methodology may be useful in organic synthesis. Further investigation in this area is being intensively carried out in our laboratory.

Experimental Section

Synthesis of Starting Materials. Tertiary 2,3-allenols were prepared from the modified Crabbé reaction of corresponding propargyl alcohols,[13] or the $LiAlH_4$ reduction of corresponding DHP-protected propargyl alcohols.[14]

Synthesis of α-Bromoallylic Ketones 3a−m: (1) 2-(1′-Bromovinyl)cycloheptanone (3a). Typical Procedure 1. To a reaction vessel were added 1-propadienylcyclohexanol **1a** (41.3 mg, 0.30 mmol), H_2O (4.0 mL), and NBS (54.8 mg, 0.31 mmol). After 2 h the starting material **1a** was completely consumed as indicated by TLC, and the resulting mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (1 mL), extracted with ether (3 × 10 mL), washed with brine (10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation afforded the crude product, which showed 60% of **3a** and 8% of **2a** with CH_2Br_2 as the internal standard according to the ^1H NMR analysis. Column chromatography on silica gel pre-eluted with pure petroleum ether then10 drops of AcOH (eluent: petroleum ether/ethyl acetate = 30/1) afforded **3a** (37.8 mg, 58%): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.70 (d, J = 1.8 Hz, 1 H), 5.58 (d, J = 1.8 Hz, 1 H), 3.45 (dd, J_1 = 10.8 Hz, J_2 = 3.3 Hz, 1 H), 2.71−2.50 (m, 2 H), 2.09−1.73 (m, 5 H), 1.62−1.28 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 131.6, 118.7, 62.2, 43.4, 30.8, 29.6, 28.3, 24.6; IR (neat) ν (cm^{-1}) 2931, 2856, 1709, 1625, 1454, 1322, 1231, 1146; MS (70 eV, EI) m/z (%) 218 (M^+(^{81}Br), 26.3), 216 (M^+(^{79}Br), 26.6), 67 (100); HRMS calcd for $C_9H_{13}O^{79}Br$ (M^+) 216.0150, found 216.0150.

(2) 2-(1′-Bromovinyl)cyclohexanone (3b). Typical Procedure 2. To a reaction tube were added MeCN (4.0 mL), H_2O (0.27 mL), 1-propadienylcyclopentanol **1b** (37.8 mg, 0.30 mmol), and NBS (54.2 mg, 0.30 mmol). After 2 h the starting material **1b** was completely consumed as indicated by TLC, and the resulting mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (1 mL), extracted with ether (3 × 10 mL), washed with brine (10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation afforded the crude product, which showed 55% of **3b** with CH_2Br_2 as the internal standard according to the ^1H NMR analysis. Column chromatography on silica gel pre-eluented with 10 drops of AcOH (eluent: petroleum ether/ether = 10/1) afforded **3b** (33.1 mg, 53%): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.69−5.64 (m, 2 H), 3.34 (dd, J_1 = 11.7 Hz, J_2 = 5.4 Hz, 1 H), 2.54−2.43 (m, 1 H), 2.40−2.27 (m, 1 H), 2.25−2.13 (m, 1 H), 2.11−1.88 (m, 3 H), 1.82−1.62 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.3, 130.5, 119.4, 60.5, 41.9, 33.2, 27.2, 24.3; IR (neat) ν (cm^{-1}) 2940, 2865, 1716, 1630, 1449, 1425, 1297, 1204, 1129, 1069; MS (70 eV, EI) m/z (%) 204 (M^+(^{81}Br), 30.4), 202 (M^+(^{79}Br), 31.3), 95 (100); HRMS calcd for $C_8H_{11}O^{81}Br$ (M^+) 203.9973, found 203.9973.

Synthesis of 1,2-Allenyl Ketones 4g−n: 3-Phenylpenta-3,4-dien-2-one (4g). Typical Procedure. The reaction of 2-phenylpenta-3,4-dien-2-ol **1g** (46.2 mg, 0.29 mmol) and NBS (53.0 mg, 0.30 mmol) in H_2O (4.0 mL) afforded **4g** (33.6 mg, 74%) (column chromatography on silica gel pre-eluted with pure petroleum ether then 10 drops of Et_3N (eluent: petroleum ether/ethyl acetate = 20/1)): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43−7.26 (m, 5 H), 5.45 (s, 2 H), 2.46 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.1, 197.1, 131.6, 128.9, 128.2, 127.7, 110.7, 80.3, 28.0; IR (neat) ν (cm^{-1}) 3057, 2980, 2927, 1948, 1922, 1684, 1599, 1494, 1447, 1415, 1357, 1277, 1232, 1133, 1074, 1019, 1002; MS (70 eV, EI) m/z (%) 159 (M^+ + 1, 11.4), 158 (M^+, 100); HRMS calcd for $C_{11}H_{10}O$ (M^+) 158.0732, found 158.0734.

Synthesis of 3-Bromo-2,5-dihydrofurans 5o−q: 3-Bromo-2,2-dimethyl-1-oxaspiro[4.4]non-3-ene (5o). Following typical procedure 2, the reaction of 1-(3-methylbuta-1,2-dienyl)cyclopentanol **1o** (45.8 mg, 0.30 mmol) and NBS (53.8 mg, 0.30 mmol) in a mixed solvent of MeCN (4.0 mL) and H_2O (0.27 mL) afforded **5o** (49.5 mg, 71%) (eluent: petroleum ether/ethyl ether = 50/1): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.78 (s, 1 H), 1.85−1.50 (m, 8 H), 1.34 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 124.2, 95.7, 87.6, 39.9, 27.7, 24.2; IR (neat) ν (cm^{-1}) 2962, 2925, 2871, 1629, 1454, 1376, 1360, 1330, 1290, 1260, 1150, 1015; MS (70 eV, EI) m/z (%) 232 (M^+(^{81}Br), 7.04), 230 (M^+(^{79}Br), 7.04), 122 (100); HRMS calcd for $C_{10}H_{15}O^{79}Br$ (M^+) 230.0306, found 230.0309.

Acknowledgment. We gratefully acknowledge the State Key Basic Research and Development Program of China

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(No. 2009CB825300). Shengming Ma is a Qiu Shi Adjunct Professor at Zhejiang University. We thank Mr. Wangqing Kong in our group for reproducing the results presented in entry 14 in Table 1 and entries 5 and 11 in Table 2.

Supporting Information Available: Complete set of experimental procedures and copies of ^{1}H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.