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Electrophilic Cyclizations of Diaryl-2,3-allenyl Ethers with *N*-Bromosuccinimide: En Route to 2-Bromonaphthalenes

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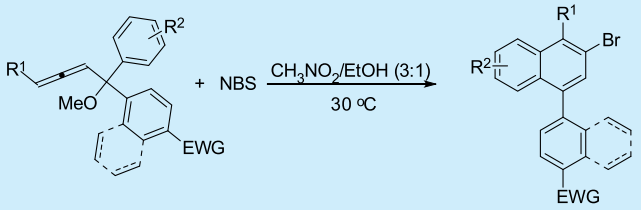
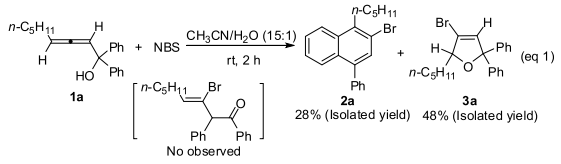
Supporting Information

ABSTRACT: The reaction of diaryl-2,3-allenyl ethers with *N*-bromosuccinimide in a mixed solvent of CH_3NO_2/EtOH affords highly functionalized 2-bromonaphthalenes in 21−66% yields. The electronic effect on the aryl is important to the selectivity of the reaction: when 4-(trifluoromethyl)phenyl or 1-naphthyl was applied as one of the two aryl groups, the regioselectivity was practical, affording the products with the other relatively electron-rich phenyl ring or the non-1-naphthyl group being cyclized as the major, respectively.



Electrophilic cyclization reactions of allenes have been well established for the synthesis of important unit in organic synthesis.[1−4] The most extensively studied ones are the electrophilic reaction of allenes with X^+ (X = Cl, Br, I, RSe), followed by the attack of intramolecular oxygen nucleophiles for the construction of the C−O bond:[5−8] The reaction of 2,3-allenols with X^+ could afford 3-halo-2,5-dihydrofurans with good to excellent yields;[5] 2,3-allenoates and 2,3-allenoic acids can also easily undergo an electrophilic cyclization reaction affording *β*-halobutenolides;[6] 4,5-dihydrofuran[7] and furan[8] derivatives were synthesized via electrophilic cyclization of allenyl ketones with electrophilic reagents; furthermore, the electrophilic cyclization could also offer an efficient strategy for the formation of aza-[9] and other heterocyclic compounds.[10] Therefore, the feasibility of using carbon nucleophiles could be an entry for the formation of C−C bonds. In 2009, the Barluenga group reported an inter- and intramolecular allene iodoarylation process involving the related C−C bond-forming processes by applying IPy_2BF_4.[11] Herein, we achieved the cyclization of diaryl-2,3-allenyl ethers with *N*-bromosuccinimide (NBS) without metal catalysis affording 2-bormonaphthalenes under mild conditions. Polysubstituted naphthalenes widely exist in numerous biologically active natural products and play an important role in medicinal chemistry research.[12] In the reported methodologies of cyclization of alkynes,[13] expensive metal catalyst is used, and the formation of more than one cycloadduct is possible for unsymmetric alkynes.

We reported the reaction of tertiary 2,3-allenoals with NBS, affording cyclic products, 3-bromo-2,5-dihydrofurans, or 1,2-shift product 3-halo-3-enones.[14] However, when 1,1-diphenyl-nona-2,3-dien-1-ol **1a** was treated with NBS in MeCN/H_2O (15:1) at room temperature, the corresponding 1,2-phenyl shift ketone product[14] was not observed: the reaction afforded a mixture of 2-bromo-1-pentyl-4-phenylnaphthalene **2a** with 28% isolated yield and 4-bromo-5-pentyl-2,2-diphenyl-2,5-dihydrofuran **3a**[5] with 48% isolated yield (eq 1), unexpectedly. After the effect of solvent on the reaction was screened, no better result was observed.



In order to avoid the formation of the cyclic bromoetherification product **3a**, the hydroxyl group in **1a** was protected as the methyl ether for the purpose of easy preparation affording the ether substrate **4a**. Thus, we started our investigation on the reaction of 1,1-diphenyl-1-methoxynona-2,3-diene **4a** with NBS. When the reaction was conducted in CH_3CN at room temperature, luckily, 2-bromo-1-pentyl-4-phenylnaphthalene **2a** was formed exclusively in 42% NMR yield as expected (Table 1, entry 1). To improve the yield of **2a**, screening of different reaction conditions was conducted: the reaction in the most commonly used solvents, such as THF, 1,4-dioxane, DMF, acetone, and DMSO, afforded **2a** in lower yields (Table 1, entries 2−7). To our delight, when CH_3NO_2 or EtOH was used as the solvent, the reaction afforded **2a** in 47% yield, exclusively (Table 1, entries 8 and 9). Then mixed solvents with different ratios of CH_3NO_2 and EtOH were used (Table 1, entries 10−13). It is exciting to observe that when the ratio of CH_3NO_2 and EtOH was 3:1, **2a** was formed in 72% NMR yield (Table 2, entry 11).

Furthermore, we studied the influence of the temperature, concentration, and loading of NBS on the reaction (Table 1, entries 14−25). Better results were achieved by running the reaction at 30 °C (Table 1, entry 20). Increasing the amount of NBS led to reduced yields, probably due to the formation of

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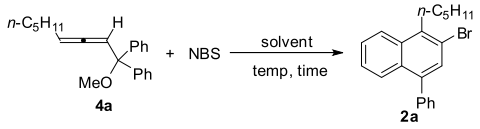
Table 1. Effect of Solvent, Temperature, and Concentration on the Reaction of 4a with NBS[a]

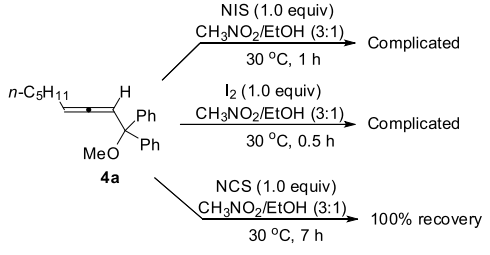


entry	solvent	temp (°C)	conc (M)	time (h)	NMR yield of **2a**[b] (%)
1	CH_3CN	rt	0.075	1.5	42
2	THF	rt	0.075	6	15
3	1,4-dioxane	rt	0.075	22	6
4	DMF	rt	0.075	22	24
5	acetone	rt	0.075	2	32
6	CH_2Cl_2	rt	0.075	5	30
7	DMSO	rt	0.075	17	28
8	EtOH	rt	0.075	6	47
9	CH_3NO_2	rt	0.075	2	47
10[c,d]	CH_3NO_2/EtOH	30	0.038	1.0	57
11[c,e]	CH_3NO_2/EtOH	30	0.056	1.0	72
12[c,f]	CH_3NO_2/EtOH	30	0.063	2.0	64
13[c,g]	CH_3NO_2/EtOH	30	0.068	1.0	60
14[e]	CH_3NO_2/EtOH	−20	0.056	3.0	37
15[e]	CH_3NO_2/EtOH	−10	0.056	2.0	63
16[e]	CH_3NO_2/EtOH	0	0.056	2.5	65
17[e]	CH_3NO_2/EtOH	10	0.056	2.0	67
18[e]	CH_3NO_2/EtOH	30	0.056	1.0	72
19[e]	CH_3NO_2/EtOH	50	0.056	1.0	58
20[e]	CH_3NO_2/EtOH	30	0.10	1.0	71 (62[h])
21[e]	CH_3NO_2/EtOH	30	0.15	1.0	61
22[e]	CH_3NO_2/EtOH	30	0.30	0.5	52
23[e]	CH_3NO_2/EtOH	30	0.025	1.0	63
24[e,i]	CH_3NO_2/EtOH	30	0.10	1.0	61
25[e,j]	CH_3NO_2/EtOH	30	0.10	1.0	61
26[e,k]	CH_3NO_2/EtOH	30	0.10	3	63
27[e,l]	CH_3NO_2/EtOH	30	0.10	6	0
28[e,m]	CH_3NO_2/EtOH	30	0.10	2	24
29[e,n]	CH_3NO_2/EtOH	30	0.10	2	0
30[e,o]	CH_3NO_2/EtOH	30	0.10	1.5	13

[a]A solution of **4a** (0.3 mmol) was treated with NBS (0.3 mmol) in the solvent (4 mL). [b]The yields were determined by ^{1}H NMR analysis with 1,3,5-trimethylbenzene as the internal standard. [c]4 mL of CH_3NO_2 was used, and the alcohol was added in volume ratio. [d]The ratio of CH_3NO_2/EtOH is 1:1. [e]The ratio of CH_3NO_2/EtOH is 3:1. [f]The ratio of CH_3NO_2/EtOH is 5:1. [g]The ratio of CH_3NO_2/EtOH is 10:1. [h]The number in parentheses is the isolated yield. [i]1.2 equiv of NBS was used. [j]1.5 equiv of NBS was used. [k]20 mol % of $ZnCl_2$ was added. [l]20 mol % of $FeCl_3{\cdot}6H_2O$ was added. [m]$CuCl_2{\cdot}2H_2O$ (20 mol %) was added. [n]1.0 equiv of K_2CO_3 was added and 88% of **4a** recovered. [o]1.0 equiv of NaOAc was added.

byproduct(s) (Table 1, entries 24 and 25). The reaction did not proceed well when an additive of Lewis acid ($ZnCl_2$, $FeCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$) or base (K_2CO_3, NaOAc) was applied (Table 1, entries 26−30). Other electrophiles were also checked for the reaction: When NIS or I_2 were used instead of NBS, respectively, the reactions were messy (Scheme 1). However, **4a** failed to react with NCS with 100% of recovery (Scheme 1).

Scheme 1. Reaction of 4a and Other Electrophilic Reagents



Thus, balanced results were achieved by running the reaction in the mixed solvent of CH_3NO_2 and EtOH (3:1) using 1.0 equiv of NBS to afford **4a** in 71% yield (62% isolated yield) (Table 1, entry 20). With this set of optimized conditions, we studied the scope of this transformation with some of the typical results presented in Table 2: the reactions preceded smoothly affording differently substituted 2-bromonaphthalenes **2a**−**g** in moderate yields (Table 2, entries 1−7). It seems important to have a non-terminal allene since the reaction of substrate **4h** with R^1 = H (Table 2, entry 8) afforded **2h** in 4% isolated yield.

To show the practicality, the reaction of 30 mmol (8.34 g) of **4c** afforded the corresponding product **2c** in 62% yield (6.08 g, eq 2). The structure was further unambiguously established by the X-ray diffraction study of **2d** (Figure 1).[15]

We envisioned that the reaction of 1,1-diaryl-2,3-allenyl ethers with two aryl groups of different electronic nature may proceed with a selectivity: which aryl group will be cyclized forming the naphthalene unit? It has been observed that the reaction of 1-methoxy-1-(*p*-methylphenyl)-1-phenylhepta-2,3-diene **4i** with NBS afforded the product **2i**/**2i′** with a selectivity of 1.4:1

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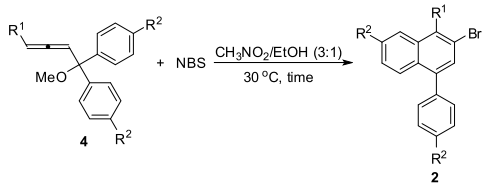
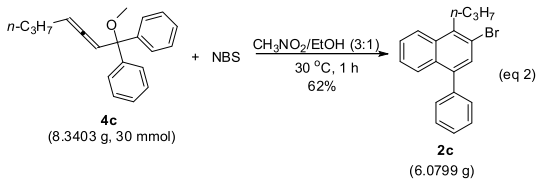
Table 2. Reaction of 1,1-Diphenyl-2,3-allenyl Methyl Ethers 4 with NBS[a]



entry	4	R^1	R^2	time (h)	2, isolated yield (%)
1	**4a**	*n*-C_5H_{11}	H	1.5	**2a**, 62
2	**4b**	*i*-C_4H_9	H	2.0	**2b**, 59
3	**4c**	*n*-C_3H_7	H	2.5	**2c**, 61
4	**4d**	CH_2CH_2Ph	H	2.0	**2d**, 66
5	**4e**	*i*-C_3H_7	H	3.0	**2e**, 51
6	**4f**	*n*-C_3H_7	Cl	5.0	**2f**, 24
7	**4g**	*n*-C_3H_7	CH_3	1.0	**2g**, 58
8	**4h**	H	H	1.5	**2h**, 4

[a]A solution of **4** (1.0 mmol), CH_3NO_2 (7.5 mL), and EtOH (2.5 mL) was treated with NBS (1.0 mmol) at 30 °C.



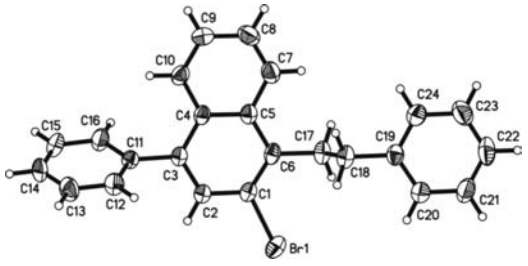
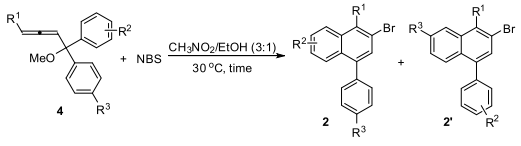


Figure 1. ORTEP presentation of **2d**.

(Table 3, entry 1). Interestingly, when a trifluoromethyl group was incorporated into one of the two aryl groups, the regioselectivity is practical, affording the products with a high ratio (≥13:1) (Table 5, entries 3−5). However, the substrate with a *p*-NO_2 substituent is not suitable for the reaction (Table 3, entry 6).

Furthermore, when one of the two phenyl rings was replaced with the 1-naphthyl group, the bromocyclization reaction occurred exclusively on the phenyl or substituted phenyl ring ring affording 3-bromo-4-propyl-1,1′-binaphthyls, exclusively (Table 4).

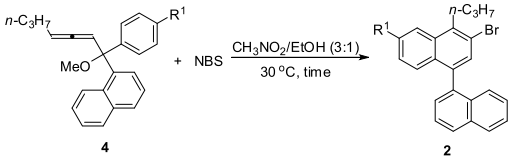
Table 3. Reaction of Diaryl 2,3-Allenyl Ethers 4 and NBS with Regioselectivity[a]



entry	4	R^1	R^2	R^3	time (h)	2/2′, isolated yield (%)
1	**4i**	*n*-Pr	4-CH_3	H	2.5	**2i**/**2i′**, 57 (1.4/1)
2	**4j**	*n*-Pr	3,5-Me_2	H	1.0	**2j**/**2j′**, 66 (2.7/1)
3	**4k**	*n*-Pr	H	CF_3	1.5	**2k**/**2k′**, 37 (13/1)
4	**4l**	Et	4-CH_3	CF_3	2.0	**2l**/**2l′**, 42 (19/1)
5	**4m**	*n*-Pr	4-OCH_3	CF_3	1.5	**2m**, 44 (>99/1)
6	**4n**	*n*-Pr	H	NO_2	2.0	complicated

[a]A solution of **4** (1.0 mmol), CH_3NO_2 (7.5 mL), and EtOH (2.5 mL) was treated with NBS (1.0 mmol) at 30 °C.

Table 4. Reaction of Diaryl 2,3-Allenyl Ether 4 with NBS[a]

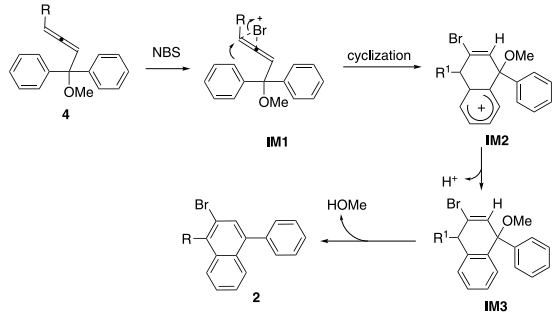


entry	4	R^1	time (h)	2, isolated yield (%)
1	**4o**	H	1.5	**2o**, 56
2	**4p**	Cl	2.0	**2p**, 29
3	**4q**	F	2.0	**2q**, 31
4	**4r**	CF_3	2.0	**2r**, 21
5	**4s**	CH_3	1.0	**2s**, 52

[a]A solution of **4** (1.0 mmol), CH_3NO_2 (7.5 mL), and EtOH (2.5 mL) was treated with NBS (1.0 mmol) at 30 °C.

A rationale is proposed for this reaction (Scheme 2).[16] First, the interaction of Br^+ with the C═C bond of the allene unit remote from the aryl groups afforded the intermediate **IM1**, which would be attacked by the aryl group affording the intermediate **IM2**. Next, the resulting cyclic carbocation of intermediate **IM2** would afford the aromatized intermediate **IM3** upon release of H^+. After elimination of HOMe, the desired product **2** would be formed.

Scheme 2. Proposed Mechanism of the Reaction



Because of the existence of the C−Br, polysubstituted naphthalenes[12] may be prepared by the well-established coupling reactions: the Suzuki coupling of **2c** with phenylboronic acid using Na_2CO_3 as base in DME and H_2O (1:1) afforded **5c** in 76% yield; the coupling of **2c** with dimethylzinc was carried out in 1,4-dioxane under the catalysis of $Pd(PPh_3)_2Cl_2$ to afford **6c** in 94% yield (Scheme 3).

In conclusion, we have developed an electrophilic cylization reaction between 1,1-diaryl-2,3-allenyl methyl ethers and NBS providing a highly efficient synthetic approach to 2-bromonaphthalenes with a nice scope, and the reaction may easily be carried out on a 30 mmol scale. For substrates with different phenyl rings, the relatively electron-rich phenyl ring was cyclized; with one of the two aryl groups being 1-naphthyl, the phenyl ring was exclusively cyclized. The coupling reaction of the C−Br bond

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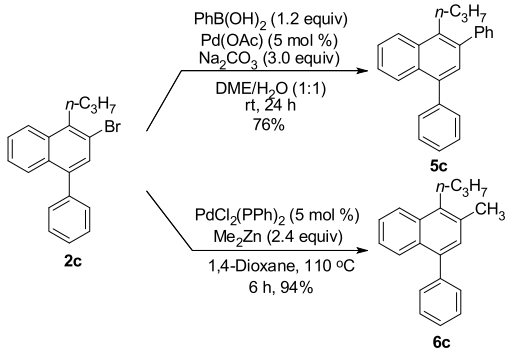
Scheme 3. Coupling Reactions of 2c



provides further opportunity for elaboration. Further studies in this area are being actively pursued in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) **2d**: $C_{24}H_{19}Br$, MW = 387.3, triclinic, space group *P*-1, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0506, wR2 = 0.0925; *R* indices (all data), R1 = 0.0830, wR2 = 0.1133; a = 9.4179 (10) Å, b = 9.9520 (12) Å, c = 11.0905 (12) Å, α = 94.288 (9)°, β = 108.773 (9)°, γ = 108.953 (10)°, V = 912.0 (2) Å^3, T = 293 (2) K, Z = 2, reflections collected/unique 5628/2345 (R_{int} = 0.0722), no. of observations [$>2\sigma(I)$] 3331, parameters: 226. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 1003917.

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