Electrophilic Cyclization of Buta-1,3-diynylarenes: Synthesis of Precursors of (*Z*)-3-Ene-1,5-diyne Systems Fused to Heterocycles

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Abstract: A simple, convenient, and promising strategy for the synthesis of 2-ethynyl-3-iodo-benzothiophenes, -benzofurans, and -indoles based on electrophilic cyclization of easily available *ortho*-functionalized (buta-1,3-diynyl)arenes was developed. The unique potential of using these compounds as starting materials for the synthesis of enediyne systems, containing thiophene, furan, and pyrrole units is demonstrated.

Key words: electrophilic cyclization, alkynes, heterocycles, enediynes

Electrophilic cyclization of ethynylarenes is well known as an efficient method for the synthesis of fused halogenated heterocycles,[1] including 3-iodobenzothiophenes,[1d,2] -benzofurans,[1b,c,i,3] and -indoles.[1e,4] These compounds are of great interest for the synthesis of a wide variety of heterocyclic compounds with special biological activity[5] and physical properties.[6]

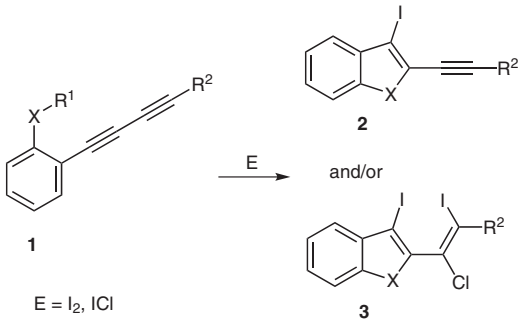
While the cyclization of *ortho*-substituted ethynylarenes was investigated in details, there are only a few examples of iodocyclization of buta-1,3-diynyl derivatives. Thus, symmetrically[1b,7] and asymmetrically[1b] substituted 1,4-diarylbutadiynes underwent a double cyclization to give symmetrical and asymmetrical bisheterocyclic compounds. The formation of 4-iodo-3-ethynylisocoumarine was also detected as an intermediate of double cyclization.[1b]

Recently, we demonstrated the Richter-type cyclization of *ortho*-(alka-1,3-diynyl)arenediazonium salts to be a short route to 3-alkynyl-4-halocinnolines.[8] Aiming at the development of a general and efficient approach towards haloethynylheterocycles, as direct precursors of enediyne systems, fused to a heterocyclic core, we reasoned that such compounds may be accessed via electrophilic cyclization of *ortho*-functionalized buta-1,3-diynyarenes. It should be noted that there is no general method to construct (*Z*)-3-ene-1,5-diyne system attached to a variety of heterocycles. Reported syntheses of such systems usually include transformation of functional groups to the ethynyl moieties[9] or double cross-coupling of terminal acetylenes with dihalosubstituted heteroarenes,[10] which are not widely accessible. Meanwhile, heterocycles possessing an enediyne system are promising objects for the medicinal chemistry as analogues of naturally occurred enediyne antibiotics, which display strong antineoplastic activity.[11]

Herein we report for the first time the electrophilic cyclization of *ortho*-buta-1,3-diynylthiophenol, -aniline, and -phenol derivatives, which led to the formation of benzannulated 2-ethynyl-3-iodo-*S*,*N*,*O*-five-membered heterocycles. Despite the fact that, Pd-, Cu-, and base-catalyzed cyclizations of buta-1,3-diynylaniline and buta-1,3-diynylphenol derivatives are convenient methods for the synthesis of 2-ethynylindoles and 2-ethynylbenzofurans,[12] no data has been reported about application of the electrophilic cyclization for the producing of this type of heterocycles, having both ethynyl and halogen moieties.

First of all, a series of *ortho*-buta-1,3-diynylthiophenol **1a–d**, -phenol **1g–i**, and *N*,*N*-dimethylaniline derivatives **1e**,**f** were obtained as the starting materials. Compounds **1a–d**,**g–i** were prepared from corresponding *ortho*-iodothiophenol or -phenol derivatives and buta-1,3-diynes by Sonogashira coupling[13a] using procedure developed in our group recently.[13b] *N*,*N*-Dimethylaniline derivatives **1e**,**f** were synthesized by methylation of corresponding *ortho*-buta-1,3-diynylaniline derivatives[13b,c] with MeI.

It was found that *ortho*-buta-1,3-diynylthioanisole derivatives **1a–c** can be efficiently converted into 2-ethynyl-3-iodobenzothiophenes **2a–c** by using of iodine in acetonitrile at room temperature (Scheme 1, Table 1, entries 1–3).



Scheme 1 Electrophilic cyclization of *ortho*-buta-1,3-diynylthiophenol (X = S), -aniline (X = NMe), and -phenol (X = O) derivatives. For R^1, R^2, see Table 1.

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It should be noted that cyclization of trimethylsilyl derivative **1d** under the same conditions gave the mixture of silylated and desilylated products **2d** and **2d′** in a molar ratio of 4.5:1 (entry 4).[14] Unfortunately, complete separation of this mixture by column chromatography could not be achieved due to the close retention times of compounds **2d** and **2d′**. However, it was possible to isolate the silylated compound **2d** in 30% yield. When the reaction was carried out in dry dichloromethane (r.t., 3 h) without treatment of the reaction mixture with aqueous $Na_2S_2O_3$ solution at the end, a mixture of **2d** and **2d′** with the molar ratio 23:1[14] was obtained (entry 5). Treatment of this mixture with K_2CO_3 in MeOH (r.t., 5 h) gave 2-ethynyl-3-iodobenzothiophene **2d′** in 50% yield. It should be noted, that this compound is extremely interesting as a substrate for the synthesis of cyclododeca-1,5,9-triene-3,7,11-triyne derivatives.[15]

Cyclization of aniline derivatives **1e**,**f** did not proceed in acetonitrile at room temperature and required a higher temperature due to the lower nucleophilicity of dimethylamino group compared to methylthio group. Thus, cyclization of *N*,*N*-dimethylamino-*ortho*-buta-1,3-diynylanilines **1e**,**f** proceeded smoothly at 40 °C (entries 6 and 7) to give 2-ethynyl-3-iodoindole derivatives **2e**,**f** in good yields.

With regard to the synthesis of 2-ethynyl-3-iodobenzofuran derivatives, we showed that iodocyclization of *ortho*-(4-phenylbuta-1,3-diynyl)anisole (**1g**) with 1 equivalent of iodine in acetonitrile at 40 °C gave the desired product **2g** in a poor yield (entry 8). Treatment of anisole **1g** with a more active electrophilic agent (iodine monochloride, 2 equiv) in dichloromethane led to the formation of byproduct **3g** with an iodochlorinated triple bond (entry 9). In the case of an equimolar ratio of reagents a mixture of **2g** and **3g** was detected by TLC and GC-MS monitoring. O-Benzylated *ortho*-dodeca-1,3-diynylphenole **1h** with iodine did not undergo cyclization even at 70 °C in acetonitrile at all, which is in accordance with the known leaving-group activities in electrophilic cyclization-type reactions.[1h] Nevertheless, we found that the use of iodine monochloride in acetonitrile is favorable for selective cyclization of O-benzylated derivative **1h**. In this case 2-ethynylbenzofurane **2g** was isolated in 49% yield (entry 10).

However, when we attempted to use iodine monochloride in acetonitrile for the cyclization of *ortho*-dodeca-1,3-diynylanisole (**1i**), the iodochlorination of the triple bond in the 3-iodo-2-decynylbenzofurane proceeded smoothly to yield the benzofurane **3i** with iodochlorinated triple bond (entry 11).[16]

Thus we demonstrated that benzannulated five-membered-*S*,*N*,*O*-heterocycles, possessing both ethynyl moiety and iodine atom, can be directly accessed via electrophilic cyclization of the corresponding functionalized *ortho*-buta-1,3-diynylarenes. The ability of *ortho*-buta-1,3-diynylthiophenol, -aniline, and phenol derivatives to undergo electrophilic cyclization is in accordance with the relative nucleophilicity of the functional groups and decreases among S > N > O.

Table 1 Synthesis of Compounds **2** and **3**

Entry	Substrate				Conditions[a]	Product, yield (%)[b]		
	1	X	R^1	R^2		R^2	**2**[19]	**3**
1	**1a**	S	Me	Ph	A	Ph	**2a** 83	–
2	**1b**	S	Me	C_8H_{17}	A	C_8H_{17}	**2b** 84	–
3	**1c**	S	Me	$(CH_2)_2OH$	A	$(CH_2)_2OH$	**2c**[20] 67	–
4	**1d**	S	Me	TMS	A	TMS H	**2d** 61 **2d′** 13	–
5	**1d**	S	Me	TMS	B	TMS H	**2d** 66 **2d′** 4	–
6	**1e**	NMe	Me	Ph	C	Ph	**2e** 75	–
7	**1f**	NMe	Me	C_8H_{17}	C	C_8H_{17}	**2f** 88	–
8	**1g**	O	Me	Ph	D	Ph	**2g** 16	–
9	**1g**	O	Me	Ph	E	Ph	**2g** traces	**3g** 59[c]
10	**1h**	O	Bn	Ph	F	Ph	**2g** 49	**3g** traces
11	**1i**	O	Me	C_8H_{17}	F	C_8H_{17}	**2i** traces	**3i** 38[c]

[a] Conditions A: I_2 (1 equiv), MeCN, r.t., 3 h. Conditions B: I_2 (1 equiv), dry CH_2Cl_2, r.t., 3 h. Conditions C: I_2 (1 equiv), MeCN, 40 °C, 5 h. Conditions D: I_2 (1 equiv), MeCN, 40 °C, overnight. Conditions E: ICl (1 equiv), CH_2Cl_2, r.t., overnight, then ICl (1 equiv), r.t., 1 h. F: ICl (1 equiv), MeCN, r.t., overnight, then ICl (0.5 equiv), r.t., 3 h.

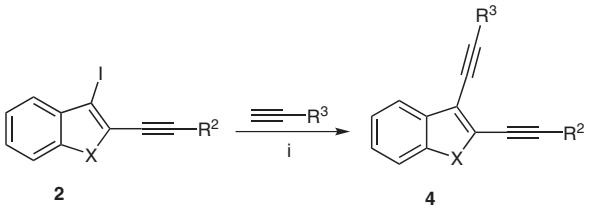
[b] All yields are given for individual compounds after purification by column chromatography; yields of **2d** and **2d′** (entries 4, 5) were calculated in accordance to the molar ratio of **2d** and **2d′** (see ref. 14), which was determined from ^{1}H NMR spectra of mixtures.

[c] Position of iodine and chlorine atoms was determined according to HMBC experiment.

Encouraged by the successful development of iodocyclization toward 3-ethynyl-2-iodoheterocycles we turned our attention to the synthesis of enediyne systems. There are a few reported examples of enediynes fused to thiophene,[1b,9,17] pyrrole,[18] and furan rings,[9] and only few known compounds with different substituents attached to the triple bonds[18a,b] because of the lack of methods for their synthesis.

So, the approach towards benzannulated 2-ethynyl-3-iodo-*S*,*N*,*O*-five-membered heterocycles described above should open a simple way for the synthesis of a variety of enediynes systems containing heterocyclic rings and different substituents attached to the triple bonds.

To explore this opportunity we synthesized several enediyne systems using the Sonogashira coupling protocol in the presence of $Pd(PPh_3)_4$ as a catalyst and diisopropanolamine (DIPA) as a base. All enediynes **4a–i** were isolated in moderate to good yields without optimization of the reaction conditions (Scheme 2, Table 2).



Scheme 2 Synthesis of benzothiophene-, indole-, and benzofuran-containing enediyne systems. *Reagents and conditions*: (i) $Pd(PPh_3)_4$, CuI, Ph_3P, DMF, DIPA, 50 °C, overnight.

Table 2 Synthesis of Enediynes **4**

Entry	Substrate			Acetylene	Product	Yield (%)
	2	X	R^2	R^3	**4**[21]	
1	**2a**	S	Ph	C_6H_{13}	**4a**	71
2	**2a**	S	Ph	$(CH_2)_3OH$	**4b**	72
3	**2a**	S	Ph	TMS	**4c**	83
4	**2b**	S	C_8H_{17}	Ph	**4d**	65
5	**2b**	S	C_8H_{17}	4-$MeOC_6H_4$	**4e**	59
6	**2c**	S	$(CH_2)_2OH$	TMS	**4f**[22]	63
7	**2f**	NMe	C_8H_{17}	Ph	**4g**	76[a]
8	**2g**	O	Ph	C_6H_{13}	**4h**	47
9	**2g**	O	Ph	TMS	**4i**	69

[a] Reaction was carried out at 40 °C.

In summary, for the first time the electrophilic cyclization of *ortho*-buta-1,3-diynylthiophenol, -aniline, and -phenol derivatives was accomplished to give benzannulated 3-iodo-2-ethynylheterocycles. This is a promising and direct approach towards heterocyclic compounds possessing iodine and ethynyl moiety at neighboring atoms, which are precursors of various enediyne systems fused to heterocyclic core.

The three-step methodology described herein enables the construction of asymmetrically substituted enediyne systems with absolute regiocontrol. We also demonstrated that these substituents may contain such functional groups as OH and TMS, which is very important for further enediyne modifications.

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(19) **General Procedure for Electrophilic Cyclization of *ortho*-Buta-1,3-diynylthiophenol, -Aniline, and -Phenol Derivatives Using I_2**
To an Ar flushed solution of corresponding *o*-(buta-1,3-diynyl)arene **1** (0.2 mmol) in MeCN (3 mL), a solution of iodine (0.2 mmol, 0.051 g,) in MeCN (2 mL) was added dropwise. The reaction mixture was stirred at corresponding temperature up to disappearance of starting material according to TLC monitoring (see Table 1). Then, the reaction mixture was diluted with 5% aq solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3 × 7 mL). The combined organic layers were washed with H_2O, dried over anhyd Na_2SO_4, and concentrated under reduced pressure to yield the crude product, which was purified by column chromatography on silica gel using pentane (**for 2a**,**b**,**d**,**e**,**g**) or cyclohexane–EtOAc (**2c**,**f**) as the eluent.
(20) **Selected Data for 2c**
Mp 73–75 °C. IR (neat): ν = 3124 (OH), 2927 (CH), 2222 (C≡C), 1449, 1427, 1370, 1326, 1294, 1243, 1192, 1158, 1062, 1031, 1016, 983, 938, 914, 849, 831, 747, 721, 707 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (t, *J* = 6.5 Hz, 1 H), 2.83 (t, *J* = 6.1 Hz, 2 H), 3.88–3.93 (m, 2 H), 7.38–7.46 (m, 2 H), 7.67–7.72 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 60.8, 87.6, 96.9, 122.1, 125.0, 125.7, 126.1, 126.4, 138.6, 140.3 (two signals are overlapping with each other). MS (EI, 70 eV): *m/z* (%) = 328.0(100) [M]$^+$, 296.9 (66) [M – CH_2OH]$^+$, 171.0(31), 139.1 (5) 126.1 (14). HRMS: *m/z* calcd for $C_{12}H_9OSI$: 327.9419. Found: 327.9418. Anal. Calcd for $C_{12}H_9OSI$: C, 43.92; H, 2.76; S, 9.77. Found: C, 43.85; H, 2.69; S, 9.61.
(21) **General Procedure for the Synthesis of Enediyne Systems 4**
To a stirred solution of 2-ethynyl-3-iodo heterocyle **2** (0.1 mmol) in DMF (2 mL), the alkyne (0.2 mmol), $Pd(PPh_3)_4$ (5 mol%), Ph_3P (10 mol%), and DIPA (0.4 mmol) were added. The reaction vial was evacuated and flushed with Ar several times. After that 15 mol% of CuI was added, the reaction vial was then sealed and flushed with Ar. The reaction mixture was allowed to stir at 40–50 °C (see Table 2) overnight. After cooling, the reaction mixture was poured into the sat. aq solution of NH_4Cl and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed two times with H_2O, dried over anhyd Na_2SO_4, and concentrated under reduced pressure to yield the crude product, which was purified by column chromatography on silica gel using pentane (for **4a**,**c**,**d**,**h**,**i**) or cyclohexane–EtOAc (for **4b**,**e**–**g**) as the eluent.
(22) **Selected Data for 4f**
IR (film on KBr): ν = 3358 (OH), 3061 (CH), 2958 (CH), 2897 (CH), 2223 (C≡C), 2149 (C≡C), 1458, 1433, 1349, 1317, 1249, 1216, 1160, 1081, 1046, 976, 938, 896, 843, 729, 687, 642 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.32 (s, 9 H), 2.02 (t, *J* = 6.7 Hz, 1 H), 2.83 (t, *J* = 6.1 Hz, 2 H), 3.85–3.90 (m, 2 H), 7.38–7.45 (m, 2 H), 7.70–7.72 (m, 1 H), 7.83–7.85 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1, 24.5, 60.8, 75.8, 97.5, 97.7, 101.5, 122.0, 122.8, 123.3, 125.1, 126.1, 127.3, 138.0, 138.5. MS–FAB: *m/z* (%) = 299.1 (61) [M$^+$ + H], 298.1 (100) [M$^+$]. HRMS: *m/z* calcd for $C_{17}H_{18}OSSi$: 298.0848; found: 298.0845.