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5-*Endo-Dig* Electrophilic Cyclization of 1,4-Disubstituted But-3-yn-1-ones: Regiocontrolled Synthesis of 2,5-Disubstituted 3-Bromo- and 3-Iodofurans

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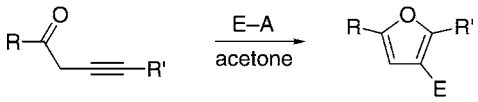
ABSTRACT



81-94%

E–A = NBS, NIS, ICl/CH_2Cl_2

5-*Endo-dig* electrophilic cyclization of 1,4-diaryl but-3-yn-1-ones with *N*-bromosuccinimide or *N*-iodosuccinimide/acetone and iodine monochloride/CH_2Cl_2, at room temperature, in the absence of base, provides 3-halo-2,5-diarylfurans with excellent regiocontrol and high yields (81–94%).

The furan unit is found in a number of natural products and synthetic materials, including industrial intermediates and pharmaceuticals. The development of synthetic routes that allow the facile assembly of substituted furans under mild conditions from simple, readily available starting materials still remains an important objective.[1] In general, substituted furans are accessed via ring derivatization or cyclization of acyclic precursors.[2] Numerous heteroannulation reactions, including transition-metal-catalyzed, leading to substituted furans have been reported.[1,3,4] Among the variety of oxygen-containing compounds that can be subjected to cyclization, unsaturated alcohols or ketones are substrates of major interest.[3a,5,6]

Halofurans are important derivatives that provide an opportunity for further functionalization. In particular, iodo- and bromofurans are useful as substrates in a variety of C−C, C−N, or C−S bond-forming reactions,[7−11] and they also serve as building blocks for combinatorial chemistry.[12] Since

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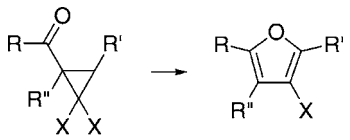
the HOMO coefficient is greater for the α-C-atoms than for the *β*-C-atoms, electrophilic reactions at the 3- or 4-position are generally more difficult than substitution at the 2- or 5-position.[13]

We have designed a homologous family of 2,5-unsymmetrically substituted 3-halofurans. The preparation of this class of compounds is a considerable synthetic challenge. Direct halogenation of 2,5-unsymmetrically (but electronically similar) substituted furans generally leads to mixtures of regioisomers.[14] Multistep sequences such as ring cleavage of *gem*-dihalocyclopropyl ketones proceed in moderate yields (Scheme 1).[7,15] Treatment of but-2-yn-4-ol-1-ones with HX (X = Br, Cl, I), typically at 50 °C, yields 3-halo-2,5-disubstituted furans.[16,17] 3-Fluoro-2,5-disubstituted furans can also be obtained via base-promoted cyclization/elimination of substituted 2,2-difluorobut-3-yn-1-ols.[18]

Scheme 1. Cyclization/Elimination of *gem*-Dihalocyclopropanes



Electrophilic cyclization of unsaturated compounds has proven to be an efficient method for the one-step construction and functionalization of furan units.[19−23] Reactions that involve the presence of a core aromatic ring such as electrophilic cyclization of *o*-alkynyl phenols[19] and acetoxy- or benzyloxypyridines[20] have been reported to yield halobenzofurans or related aromatic compounds. Additionally, iodocyclization of alk-3-yn-1,2-diols followed by dehydration in the presence of base yields 3-iodofurans derivatives.[21] We recently reported the electrophilic heteroannulation of 5-alkynyl-2′-deoxyuridines to furanopyrimidine nucleosides.[24] In this case, amido−iminol tautomerization and the presence of an sp^2 carbon in the core may facilitate the cyclization. Presently, in pursuit of a regiocontrolled synthesis of 2,5-unsymmetrically substituted 3-halofurans, we have isolated the furan acyclic precursor core (but-3-yn-1-one) with various aromatic endgroups. Phenyl, *p*-alkylphenyls, and *p*-halophenyls were selected as aryl substituents. We have focused on easily handled *N*-halosuccinimides, which have literature precedents in electrophilic halocycloisomerizations.[22a,24,25]

Our new route to 2,5-substituted 3-halofurans started from commercially available styrene oxide or its derivatives (**1a**−**c**), as presented in Scheme 2. Terminal alkynes (**2a**,**b**) (1.5 equiv) were deprotonated with LDA (1.5 equiv) in DMSO, as previously described;[26] THF and DMF were inefficient solvents for this protocol. Ring opening of the epoxides proceeded with full regioselectivity as confirmed by ^{1}H NMR to yield, after workup, 2,5-diarylbut-3-yn-1-ols (**3a**−**e**).

Reaction of the alkynyl alcohol **3b** with electrophiles such as *N*-iodosuccinimide (NIS) or *N*-bromosuccinimide (NBS)

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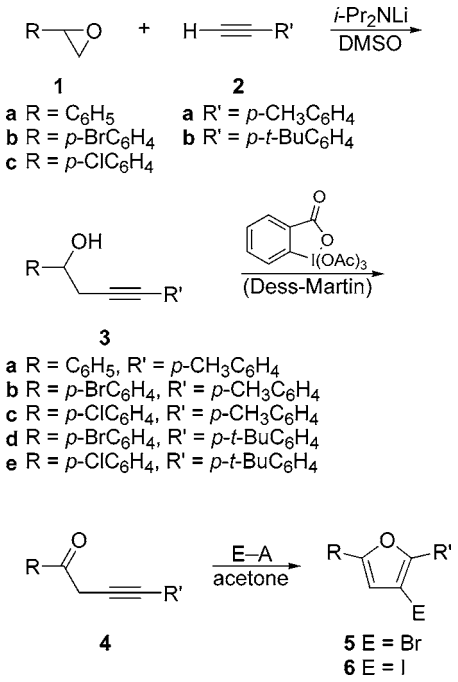
Scheme 2. Synthesis of Halofurans **5** and **6**



(2 equiv, acetone), in the absence of base, showed no conversion after 48 h at room temperature. It has been reported that relevant reaction of but-3-yn-1-ols with elemental iodine in the presence of a base leads to the 1,2-iodine addition product.[27] Thus, the isolated butynols **3a**−**e** were treated with Dess−Martin reagent[28] (1.5 equiv) in CH_2Cl_2 at room temperature (1 h) to yield but-3-yn-1-ones (**4a**−**e**, Scheme 2). Alternative oxidation with MnO_2 (8 equiv, 42 h, CH_2Cl_2) did not show satisfactory progress of the reaction. Subsequently, the isolated alkynyl ketones **4a**−**e** were subjected to the reaction with various halogenating electrophiles.

1-Phenyl-4-(*p*-tolyl)butynone **4a** was treated with NBS (1.05 equiv) in acetone at room temperature, and complete conversion into **5a** was observed after 2 h. Since it is known that substituted furans undergo oxidative ring opening with NBS in acetone in the presence of pyridine,[29] and to maintain mild reaction conditions, all reactions were carried out in the absence of base. 3-Bromofuran **5a** was isolated, after workup, in 89% yield (Table 1). Alkynone **4a** was also treated with NIS in a similar manner to access the iodo derivative **6a** and to compare the reactivity of **4a** toward analogous halosuccinimide. Practically no difference was observed in terms of rate of the reaction of NBS vs NIS, as opposed to different reactivity toward 5-alkynyl uridines.[24]

The utility of a stronger electrophile, iodine monochloride, was also examined for the cycloisomerization of **4a**. The reaction conditions included CH_2Cl_2 and 1.05 equiv of ICl. Similarly, the derived product **6a** was formed at room temperature.

Table 1. Preparation of Halofurans **5** and **6** via Cycloisomerization of **4**

butynone	R	R′	reagent (E−A), solvent[a]	halofuran	yield (%)
4a	C_6H_5	*p*-$CH_3C_6H_4$	NBS, acetone	**5a**	89
			NIS, acetone	**6a**	84
			ICl, CH_2Cl_2	**6a**	82
4b	*p*-BrC_6H_4	*p*-$CH_3C_6H_4$	NBS, acetone	**5b**	89
			NIS, acetone	**6b**	86
4c	*p*-ClC_6H_4	*p*-$CH_3C_6H_4$	NBS, acetone	**5c**	83
			NIS, acetone	**6c**	94
4d	*p*-BrC_6H_4	*p*-*t*-BuC_6H_4	NBS, acetone	**5d**	87
			NIS, acetone	**6d**	81
4e	*p*-ClC_6H_4	*p*-*t*-BuC_6H_4	NBS, acetone	**5e**	86
			NIS, acetone	**6e**	88

[a] Reactions were carried out on ca. 0.6−1.4 mmol scale with 1.05 equiv of electrophilic reagent (E−A) at room temperature. For a representative procedure see ref 31.

GC/MS examination of postreaction mixtures of butynone **4a** with ICl, butynone **4b** with NBS or NIS, and **4d** with NIS indicated conversion to the halofurans **6a**/**5b**/**6b**/**6d** with 97/96/99+/99+% yields, respectively. In all reported cases in Table 1, quantitative conversion of substrate was confirmed by ^{1}H NMR. After reaction completion, the solid products were separated from the major part of spent and unreacted *N*-succinimides by extraction with ether.[30] Subsequent silica gel filtration (to remove traces of the remaining *N*-succinimides) gave halofurans **5a**−**e** and **6a**−**e** with 81−94% yield.[31] The results are summarized in Table 1.

The substituted halofurans were characterized by ^{1}H and ^{13}C NMR, IR, MS, and UV−vis spectroscopy. The characteristic NMR[32] ($CDCl_3$) features for **5a**−**e** and **6a**−**e** include the ^{1}H H-4 signal (6.77−6.79 and 6.83−6.85 ppm) and ^{13}C of C-halogen (C-3, 97.5−97.6 and 62.3−62.4 ppm) for bromo and iodo derivatives, respectively. Mass spectra for **5a**−**e** and **6a**−**e** exhibited intense molecular ions with appropriate isotope patterns characteristic for halogens, when applicable. The UV spectra were similar to those reported for relevant 2,5-diarylfurans.[33] Almost all iodo- and bromofurans gave highly accurate (±0.1%) elemental analyses.

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(30) Anhydrous (commercial) ether was used. Extraction with reagent grade ether leads to the "leaching" of the succinimide likely due to water and ethanol contents. This step is obviously not necessary for reaction with ICl.

(31) A round-bottom flask was charged with **4a** (0.200 g, 0.854 mmol) and acetone (9 mL). NBS (0.160 g, 0.900 mmol) in acetone (9 mL) was added dropwise by a syringe. The solution was stirred under nitrogen atmosphere at room temperature for 2 h. TLC showed complete conversion of substrate. Solvent was removed by rotary evaporation and the residue was extracted with ether. The solid was filtered off. The solvent was removed by rotary evaporation. Short path silica gel column chromatography (2.5 × 15 cm; $CHCl_3$) gave a colorless fraction. Solvent was removed by rotary evaporation and the residue was dried by oil vacuum pump to give **5a** as a white solid (0.238 g, 0.760 mmol, 89%). The compound can be recrystallized from methanol.

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Relevant electrophilic cyclizations are believed to proceed through an intramolecular, stepwise mechanism involving a cationic intermediate.[20,34] However, we presume that α-hydrogen abstraction may also be a mechanistic option.[35]

A molecular structure of a representative halofuran was determined by X-ray crystallography. Crystallization of compound **5e** from ether/methanol (7:3) gave single crystals suitable for X-ray analysis.[36] Inspection of Figure 1 reveals the molecular structure of the expected 3-bromofuran. Excluding the *tert*-butyl fragment, the entire molecule of **5e** is planar within 0.173 Å. The maximum atom deviations from the average plane are 0.39(1) and 0.36(1) Å for C10 and C11, respectively. Interestingly, the C═C bond of **5e** with the bromine atom attached [C2−C3, 1.377(11) Å] is significantly elongated compared to the hydrogen-substituted C4−C5 bond [1.344(10) Å].

In summary, we have demonstrated that electrophilic cyclization of but-3-yn-1-ones with various electrophilic halogen sources yields halofurans under exceptionally mild conditions: in the absence of base and in one of the most environmentally friendly organic solvents, acetone. Combining C−O and C-electrophile bond formation maximizes reaction efficiency with good atom economy; a cycloisomerization catalyst is at the same time a halogen donor. Our simple isolation protocol facilitates high yields. Our approach allows for excellent regiocontrol in the preparation of unsymmetrically 2,5-disubstituted 3-halofurans.

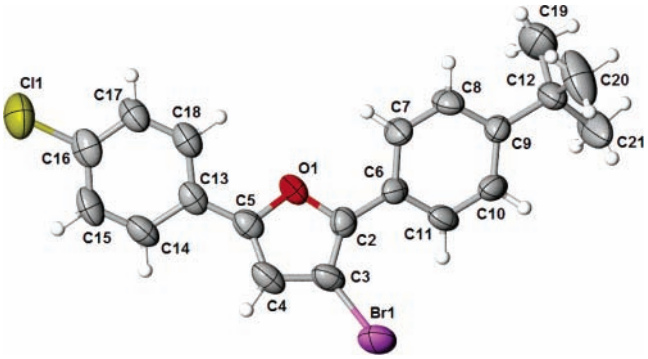

Figure 1. ORTEP view of **5e** with an atom-labeling scheme. Thermal ellipsoids at the 50% probability level. Selected interatomic distances (Å): Br1−C3 1.849(9); O1−C2 1.391(8); O1−C5 1.374(9); C2−C3 1.377(11); C2−C6 1.437(11); C3−C4 1.419(10); C4−C5 1.344(10); C5−C13 1.428(11). Key angles (deg): C2−O1−C5 109.5(7); O1−C2−C3 106.9(7); O1−C2−C6 115.1(7); C3−C2−C6 138.0(8); C2−C3−C4 106.9(7); Br1−C3−C2 126.4(7); Br1−C3−C4 126.7(6); C3−C4−C5 109.1(7); O1−C5−C4 107.6(7); O1−C5−C13 117.8(7); C4−C5−C13 134.6(8).

Acknowledgment. We thank the Oakland University Research Excellence Program in Biotechnology for support of this research.

Supporting Information Available: Synthetic procedures, analytical and spectral characterization data, ^{1}H and ^{13}C NMR spectra for all halofurans (**5a**−**e**, **6a**−**e**), and X-ray tables for **5e** and a separate CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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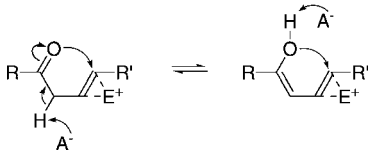
(35) A mechanistic pathway may include cyclization followed by a deprotonation (right structure) or α-hydrogen abstraction (left structure).



(36) Crystallographic data (excluding structural factors) for the structure reported in this paper were also deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-265867. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44(0)1223-336033.