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Benzannulation of Triynes Initiated by an Alder-Ene Reaction and Subsequent Trifluoromethylthiolate Addition

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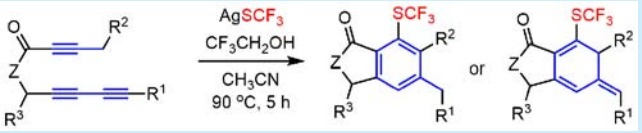
Supporting Information

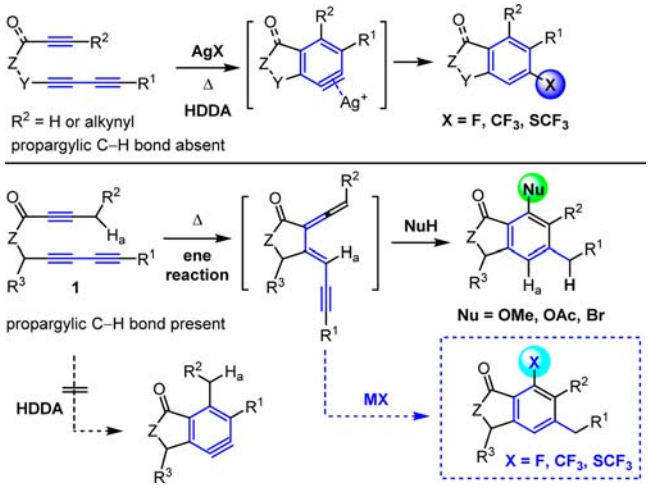
ABSTRACT: A new benzannulation reaction with accompanied trifluoromethylthiolation is described. This benzannulation can generate a range of trifluoromethylthiolated benzolactams and benzolactones from 1,3,8-triynes and a stoichiometric amount of $AgSCF_3$ at 90 °C through an initial Alder-ene reaction, 1,4-addition of $AgSCF_3$, and a series of bond-reorganization processes that include double bond migration, 6π-electrocyclization, and a [1,3]-H shift. For certain substrates containing a triisopropylsilyl (TIPS) group, the final [1,3]-H shift-interrupted products, were obtained.



Trifluoromethythiolated arenes represent an intriguing structural motif in the fields of pharmaceuticals and agrochemicals due to their unique physical and biological properties.[1] In medicinal chemistry, for example, the introduction of electron-withdrawing trifluoromethylthio group into various frameworks of drug candidates often improves their metabolic stability and lipophilicity.[2] Moreover, aryl trifluoromethylthioethers are key intermediates for the synthesis of trifluoromethyl sulfoxides and sulfones.[1] Traditionally, however, direct access to trifluoromethylthiolated arenes has been limited due to the lack of efficient synthetic methods as well as safe reagents. Accordingly, recent years have witnessed explosive interest in developing facile methods that incorporate an SCF_3 group into aromatic compounds.[3−7] Since Buchwald's pioneering example of palladium catalyzed formation of Ar−SCF_3 from aryl bromide and $AgSCF_3$,[4] other research groups have developed cross-coupling methods employing aryl halides[5] or aryl boronic acids.[6] The advent of these transition-metal-catalyzed cross-coupling strategies has facilitated the synthesis of a range of trifluoromethylthiolated arenes in recent years. On the other hand, Daugulis reported trifluoromethylation through directing group-assisted C−H bond functionalization of arenes.[7] While these strategies can selectively introduce the SCF_3 group into the positions that are not naturally reactive, prefunctionalization of aromatic compounds or installation of directing groups is typically required.

Previously we reported fluorination, trifluoromethylation, and trifluoromethylthiolation of arynes generated from bis-1,3-diynes (Scheme 1).[3e] The naissance of this aryne functionalization relies on the hexadehydro Diels−Alder (HDDA) reaction,[3e,8−14] which leads to a range of Ar−F, Ar−CF_3, and Ar−SCF_3 products. Although effective, the scope of this HDDA-based approach is limited to substrates containing bis-1,3-diynes. Even though certain triynes are known to undergo

Scheme 1. Modes of Benzannulations of Multiynes



the HDDA reaction efficiently, most of them failed to yield the expected fluorinated products. While exploring other structural types of substrates with such a limitation, we discovered an alternative benzannulation of triynes of type **1**. The products of this new benzannulation could incorporate MeOH, AcOH, and HBr,[15] which was initiated by the initial Alder-ene reaction. The kinetic preference for the Alder-ene (E_a = 33.5 kcal/mol) over HDDA (E_a = 38.1 kcal/mol) reaction was also verified by DFT calculations.[15] In conjunction with expanding the scope of the trapping of the allene−enyne intermediate, we became interested in employing nucleophiles such ^-F, $^-CF_3$, and $^-SCF_3$ that carry a countercation other than a proton. Herein

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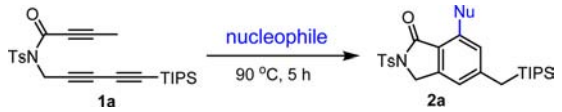
we report the successful trapping of an allene−enyne intermediate with $AgSCF_3$, which leads to the formation of trifluoromethylthiolated benzolactams and benzolactones, as well as several nonaromatic compounds.

We commenced our investigation by examining the reactivity of a number of different reagents providing nucleophiles of ^-F, $^-CF_3$, or $^-SCF_3$ together with the 1,3,8-triyne **1a** at 90 °C (Table 1). First $AgBF_4$ was chosen for fluorination based on the

Table 1. Optimization of Reaction Conditions for Ar−F, Ar−CF_3, and Ar−SCF_3 Formation



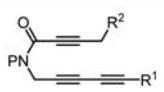
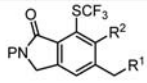
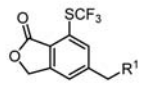
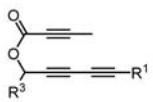
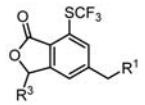
entry	nucleophile	solvent	Nu	yield (%)
1	$AgBF_4$	CH_3CN	F	0
2	AgF	CH_3CN	F	0
3	HF-Pyridine	CH_3CN	F	0
4	$(^nBu)_4NF$	CH_3CN	F	0
5	$AgCF_3$	CH_3CN	CF_3	~10
6	$AgCF_3$	toluene	CF_3	0
7	$CuCF_3$	CH_3CN	CF_3	0
8	$Zn(CF_3)_2$	CH_3CN	CF_3	0
9	$[(phen)CuCF_3]$	CH_3CN	CF_3	0
10	$[(Ph_3P)CuCF_3]$	CH_3CN	CF_3	0
11	$K[B(OMe)_3CF_3]$	CH_3CN	CF_3	0
12	$AgSCF_3$	CH_3CN	SCF_3	53
13[a]	$AgSCF_3$	CH_3CN	SCF_3	71
14[a]	$AgSCF_3$	toluene	SCF_3	13
15[a]	$AgSCF_3$	CH_2Cl_2	SCF_3	0
16[a]	$CuSCF_3$	CH_3CN	SCF_3	0

[a]Reactions were performed with CF_3CH_2OH (3 equiv).

previous fluorination of arynes generated from tetraynes.[3e] However, from this reaction no fluorination product was observed (entry 1). Other common nucleophilic fluorinating reagents such as AgF, HF-pyridine, and tetrabutylammonium fluoride (TBAF) also did not afford any desired fluorination product; instead most of the starting materials were decomposed (entries 2−4). The reaction with $AgCF_3$ generated in situ from Ruppert's reagent ($TMSCF_3$) and AgF in acetonitrile produced a meaningful amount (~10%) of trifluoromethylation product (entry 5). An analogous reaction in a nonpolar solvent failed (toluene, entries 6). Several attempts with trifluoromethylating reagents containing different counter cations were found to be ineffective (entries 7−11). Gratifyingly, treatment of **1a** with $AgSCF_3$ in CH_3CN afforded the expected product **2a** in 53% yield (entry 12). We anticipated that the presence of a proton source should be beneficial. Indeed the addition of CF_3CH_2OH (3 equiv) to the reaction improved the yield to 71% (entry 13). Reactions in other solvents such as toluene (10%) and CH_2Cl_2 (0%) provided low or no yield of the desired product under otherwise identical conditions (entries 14 and 15). Trifluoromethylthiolation with $CuSCF_3$ did not provide **2a** (entry 16).

Having established the optimized conditions for trifluoromethylthiolation, we then explored the scope of the reaction with structurally diverse 1,3,8-triynes having an amide or an ester tether (Table 2). In general, the efficiency of this trifluoromethylthiolation depends on the tether (Z = NTs, NPh, O), the silyl substituent R^1 on the 1,3-diyne, and the

Table 2. Reaction Scope of Trifluoromethylthiolation Using $AgSCF_3$[a]

entry	substrate	product	yield (%)[b]
			
1	**1a**, R^1=TIPS, R^2=H, P=Ts	**2a**	71
2	**1b**, R^1=TBDPS, R^2=Me, P=Ts	**2b**	35
3	**1c**, R^1=TIPS, R^2=H, P=Ph	**2c**	0
			
4	**1d**, R^1=TBS	**2d**	56
5	**1e**, R^1=TIPS	**2e**	75
			
6	**1f**, R^1=TBS , R^3=CH_2CH_2Ph	**2f**	67
7	**1g**, R^1=TBS , R^3=^{i}Pr	**2g**	59
8	**1h**, R^1=TBS , R^3=Ph	**2h**	64
9	**1i**, R^1=TIPS, R^3=4-F-Ph	**2i**	35
10	**1j**, R^1=TIPS, R^3=$(CH_2)_2CH=CH_2$	**2j**	67
11	**1k**, R^1=TIPS, R^3=CH_2OTBS	**2k**	59

[a]Reaction conditions: Substrates (0.1 mmol), $AgSCF_3$ (1.5 equiv), CF_3CH_2OH (3 equiv), CH_3CN (5 mL), 90 °C, 5 h. [b]Isolated yield.

propargylic substituent R^2 and R^3. While the substrate **1a** containing a methyl group (R^2 = H), derived from 2-butynoic acid, afforded the trifluoromethylthiolation product **2a** in 71% yield (entry 1), a similar substrate **1b** possessing an ethyl group (R^2 = CH_3), derived from 2-pentynoic acid, provided a significantly diminished yield (35%) most likely because of the sterically congested environment of the resulting product (entry 2). Moreover, replacing the Ts group on the nitrogen of an amide linkage with a phenyl group in **1c** completely abrogated the formation of desired product **2c** (entry 3). Though substrate **1d** bearing an ester tether provided the trifluoromethylthiolation product **2d** in 56% yield (entry 4), the corresponding substrate **1e** with a TIPS group on the 1,3-diyne provided significantly improved yield (entry 5). Substrates **1f** and **1g** with a linear (R^3 = CH_2CH_2Ph) and a branched alkyl (R^3 = *i*-Pr) group produced desired products **2f** and **2g** in 67% and 59% yield, respectively (entries 6−7). Phenyl-substituted triyne **1h** also provided the expected product **2h** in 64% yield (entry 8), however, switching the phenyl group to a more electron-withdrawing 4-fluorophenyl group in **1i** significantly diminished the yield of **2i** to 35% (entry 9). Alkenyl and silyloxy substituents in substrates **1j** and **1k** did not interfere with the trifluoromethylthiolation and, thus, afforded the desired products **2j** and **2k** in 67% and 59% yield, respectively (entries 10−11).

On the basis of the mechanistic insight gained from previous studies,[15] we surmised that the current trifluoromethylthiolation should follow similar mechanistic steps, where $^-SCF_3$ attacks the allenic carbon of the allene-enyne intermediate **A** generated via an initial Alder-ene reaction[16] (Scheme 2). A series of double-bond migrations to form 1,2,4,6-tetraene followed by a 6π-electrocyclization would lead to a penultimate intermediate **B**, which then undergoes a formal [1,3]-H shift to deliver the observed final product.

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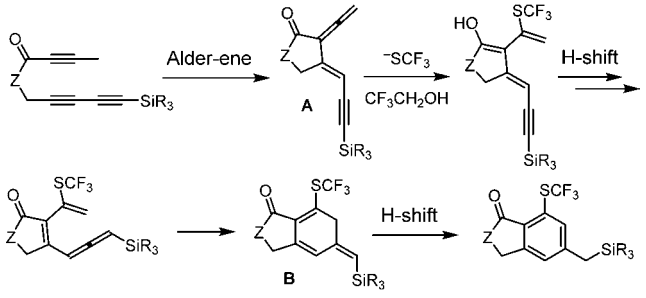
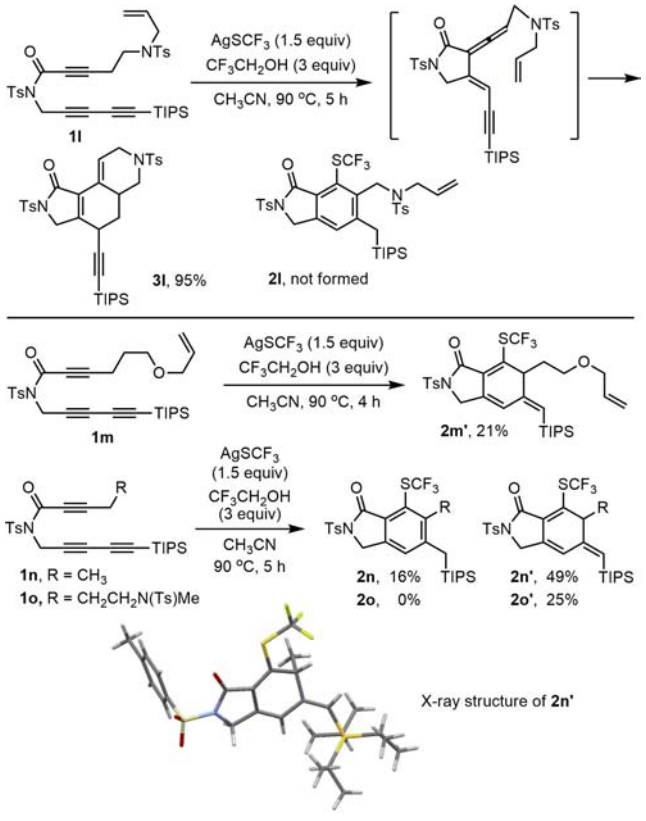
Scheme 2. Proposed Reaction Mechanism for Trifluoromethylthiolation



To gain further evidence of the involvement of an Alder-ene reaction, an appropriate alkene-tethered substrate **1l** was examined, with an expectation that the putative allene-enyne intermediate,[17] if formed, may undergo an intramolecular Diels–Alder reaction before it reacts with an external nucleophile (Scheme 3).[16,18] Indeed, the reaction of **1l** cleanly

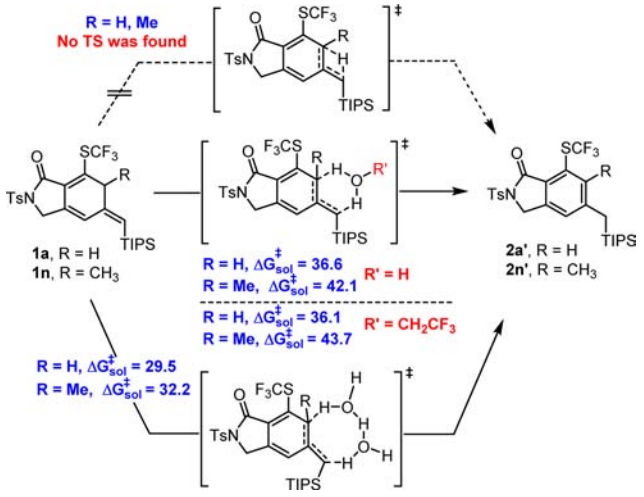
Scheme 3. Intramolecular Diels–Alder Reaction vs Conjugate Addition of $AgSCF_3$



generated product **3l**, and the trifluoromethylthiolation product was not detected. However, a closely related substrate **1m** provided neither the Diels–Alder product nor the aromatized product, instead the [1,3]-H shift-interrupted compound **2m′**, which upon heating in CD_3CN at 90 °C for 4 h aromatized quantitatively.[19] To gain more insight into this nonaromatic compound, substrates **1n** and **1o** were also examined. Under the typical reaction conditions, substrate **1n** (R = Me) produced a 1:3 mixture of **2n** and **2n′**, whereas substrate **1o** containing a slightly larger R group (R = CH_2CH_2NTsMe) provided **2o′** as a single product with a much lower yield (25%). A careful inspection of the X-ray structure of **2n′** provides a plausible clue to the existence of this nonaromatic form. In **2n′**, the CF_3 group on the sulfur occupies the opposite side of the carbonyl group,[20] which forces the adjacent methyl group to be nearly perpendicular to the cyclohexadiene ring, placing the 3° hydrogen orthogonal to the π-system of the *exo*-double bond. The unique structural feature renders the [1,3]-H shift relatively difficult, and the effect of this structural attribute becomes more significant with a larger R group on the cyclohexadiene ring.

To gain further insight into the propensity of a [1,3]-H shift, we performed brief DFT calculations for the model compounds **1a** and **1n** (Scheme 4). Calculations indicate that the transition

Scheme 4. Transition State Energies (kcal/mol) for [1,3]-H Shift (PCM-M06/6-311++G(d,p)//B3LYP/6-31G(d))



state (TS) of a direct [1,3]-H shift cannot be even located, thus a water- or alcohol-mediated process should be operating. For the TS of a bimolecular process with one molecule of water or trifluoroethanol, **1a** has a significantly lower activation barrier to reach the TS than that of **1n**. Even a significantly lower energy was calculated for the TS involving two molecules of water, where **1a** still has a 2.7 kcal/mol lower activation barrier than **1n**.

In conclusion, we have developed a benzannulation reaction to form trifluoromethylthiolated benzolactam and benzolactone derivatives from 1,3,8-triynes and $AgSCF_3$. Mechanistic evidence suggests that the conjugate addition of $^{-}SCF_3$ to an allene–enyne intermediate formed via an Alder-ene reaction, followed by double-bond migrations to generate a diene–allene intermediate. Subsequent 6π-electrocyclizaion and a formal [1,3]-H shift delivers the product. In certain cases, [1,3]-H shift-interrupted nonaromatic products were isolated. Considering the prevalent occurrence of benzolactams and benzolactones in biologically active compounds, this new benzannulation method involving concurrent trifluoromethylthiolation should find useful applications especially in the field of drug discovery and pharmaceutical synthesis.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental details, characterization data, NMR spectra (PDF)
CIF file for the X-ray structure of **2n′** (CIF)

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Notes

The authors declare no competing financial interest.

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