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Tandem Michael addition–carbene insertion reaction of 1-alkynyl(aryl)(tetrafluoroborato)-λ^3-bromanes: 1-(phenylsulfonyl)- and 1-(trifluoromethylsulfonyl)cyclopentene annulation

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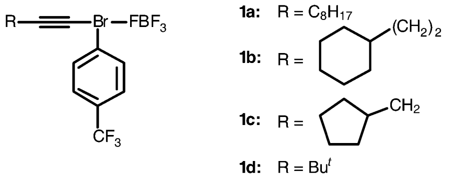
Exposure of 1-alkynyl[*p*-(trifluoromethyl)phenyl](tetrafluoroborato)-λ^3-bromanes to sodium benzenesulfinate or sodium trifluoromethanesulfinate in dichloromethane at 0 °C under argon resulted in tandem Michael–carbene insertion reactions to produce 1-sulfonylcyclopentenes selectively, with concomitant formation of a small amount of rearranged 1-alkynyl sulfones.

Hypervalent 1-alkynyl(phenyl)(tetrafluoroborato)-λ^3-iodanes are highly electron-deficient species,[1] because of the powerful electron-withdrawing nature of the phenyl(tetrafluoroborato)-λ^3-iodanyl group with a very large Hammett substituent constant (σ_p) of 1.37.[2] Hence, they serve as excellent Michael acceptors for a variety of soft nucleophiles, including stable enolates of 1,3-dicarbonyl compounds, carboxylates, phenoxides, azides, sulfinates, thiolates, thiocyanates, halides, phosphates, amides, phosphines, and arsines.[1] Because of the excellent nucleofugality of the phenyl-λ^3-iodanyl groups,[3] the Michael additions are generally followed by the reductive elimination of λ^3-iodanyl groups in the resulting vinyliodonium ylides, which generates reactive alkylidene carbenes.

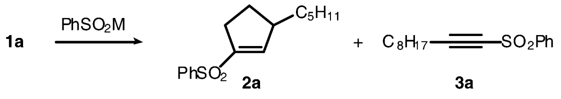


Recently, we reported the first synthesis of the related group 17 1-alkynyl-λ^3-bromanes **1**;[4] the method involves a BF_3-catalyzed ligand exchange of [*p*-(trifluoromethyl)phenyl](difluoro)-λ^3-bromane[5] with 1-alkynyl(trimethyl)stannanes in dichloromethane and affords 1-alkynyl[*p*-(trifluoromethyl)phenyl](tetrafluoroborato)-λ^3-bromanes **1** in good yields. 1-Alkynyl-λ^3-bromanes **1** should serve as more efficient Michael acceptors toward the attack of nucleophiles than the iodine analogues, 1-alkynyl-λ^3-iodanes, because of a greater Hammett substituent constant ($\sigma_p = 1.63$ for $PhBrBF_4$) of λ^3-bromanyl groups.[6] In fact, a weakly nucleophilic *p*-toluenesulfonate anion does not undergo Michael addition toward 1-alkynyl(phenyl)-λ^3-iodanes,[7] while the anion attacks the β-acetylenic carbon atom of 1-alkynyl-λ^3-bromanes **1** under mild conditions to give 1-alkynyl tosylates.[4] Formation of 1-alkynyl tosylates probably involves the intermediacy of free alkylidene carbenes, produced by Michael addition of a tosylate anion and the subsequent reductive elimination of the *p*-(trifluoromethyl)phenyl-λ^3-bromanyl group. 1,2-Shift of a tosyloxy group in the alkylidene carbenes produces 1-alkynyl tosylates. We report herein a tandem Michael–carbene insertion (MCI) reaction between 1-alkynyl-λ^3-bromanes **1** and sodium benzenesulfinate, which produces 1-(phenylsulfonyl)cyclopentenes **2** selectively under mild conditions. The reaction competes with the formation of a small amount of the rearranged alkynyl sulfones **3**.

When the reaction of 1-decynyl[*p*-(trifluoromethyl)phenyl](tetrafluoroborato)-λ^3-bromane (**1a**) (1.5 equiv.) with anhydrous sodium benzenesulfinate was carried out in benzene at room temperature for 1 h, 1-(phenylsulfonyl)cyclopentene **2a** was obtained in 53% yield, along with the formation of a small amount of 1-decynyl phenyl sulfone (**3a**) (18%) (Scheme 1 and Table 1, entry 1). Use of chloroform or dichloromethane as a solvent at 0 °C increased the yields of the products with a slightly increased selectively for **2a** (entries 2 and 3).† In THF, a higher selectivity (90%) for the formation of **2a** was observed, but with a low yield (35%); under the conditions, comparable results were obtained when 1-decynyl(phenyl)(tetrafluoroborato)-λ^3-iodane was used instead of **1a**.[8] Use of tetrabutylammonium benzenesulfinate in THF improved the yield up to 59% (entry 6). 1-Decynyl-λ^3-bromane **1a** is susceptible to hydrolysis with water, yielding 1-hydroxy-2-decanone; however, exposure of **1a** to sodium benzenesulfinate in water at 0 °C gave a 72 : 28 mixture of **2a** and **3a** in 63% yield.

Tandem Michael–carbene insertion and rearrangement reactions between 4-cyclohexyl-1-butynyl-λ^3-bromane **1b** and sodium benzenesulfinate in dichloromethane at 0 °C afforded a mixture of the spiro cyclopentene **2b** and the alkynyl sulfone **3b** in a 67 : 33 ratio (Scheme 2). High selectivity (96%) for cyclopentene formation was observed in the reaction of 3-cyclopentyl-1-propynyl-λ^3-bromane **1c**, which produced 3-(phenylsulfonyl)bicyclo[3.3.0]oct-2-ene (**2c**) in 86% yield. On the other hand, the reaction with 3,3-dimethyl-1-butynyl-λ^3-bromane **1d** selectively afforded 1-alkynyl phenyl sulfone **3d** in 84% yield. Vinyl sulfones serve efficiently as both Michael acceptors and as 2π partners in cycloaddition reactions,[9] and 1-(phenylsulfonyl)cyclopentenes have been shown to be useful intermediates for the synthesis of complex natural products.[10]

Since the trifluoromethylsulfonyl group is one of the strongest electron-withdrawing substituents with a large Hammett σ_p constant of 0.96,[11] syntheses of 1-(trifluoromethylsulfonyl)cyclopentenes are of great interest. Reaction of the λ^3-bromane **1a** with

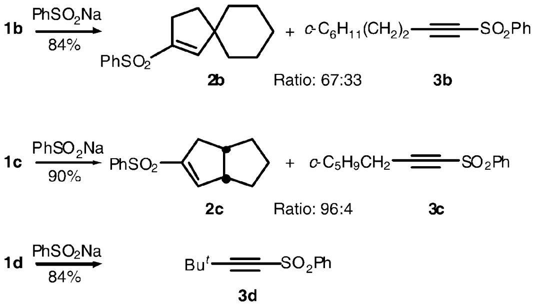


Scheme 1

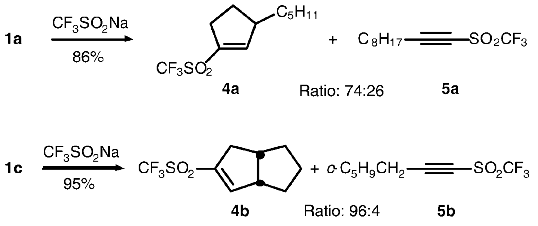
Table 1 Reaction of 1-decynyl-λ^3-bromane **1a** with benzenesulfinates[a]

Entry	M	Solvent	Yield/%[b]	**2a** : **3a**[c]
1	Na	PhH[d]	71	74 : 26
2	Na	$CHCl_3$	88	75 : 25
3	Na	CH_2Cl_2	86	79 : 21
4	Bu_4N	CH_2Cl_2	86	76 : 24
5	Na	THF	35	90 : 10
6	Bu_4N	THF	59	86 : 14
7	Na	H_2O	63	72 : 28

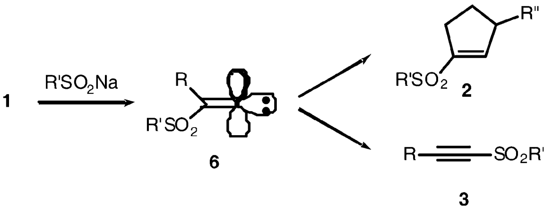
[a] Unless otherwise noted, reactions were carried out using 1-decynyl-λ^3-bromane **1a** (1.5 equiv.) at 0 °C for 1 h under argon. [b] Total isolated yields of **2a** and **3a**. [c] Determined by ^1H NMR of the crude reaction mixture. [d] Reaction was carried out at room temperature.



Scheme 2 Conditions: λ^3-bromane (1.5 equiv.), $PhSO_2Na$, CH_2Cl_2, 0 °C, 1 h, Ar.



Scheme 3 Conditions: λ^3-bromane (1.6 equiv.), CF_3SO_2Na, CH_2Cl_2, 0 °C, 5 h, Ar.



Scheme 4

sodium trifluoromethanesulfinate (triflinate) under comparable conditions resulted in the formation of a mixture of vinyl trifluoromethylsulfone (triflone) **4a**‡ and 1-alkynyl triflone **5a** in a ratio of 74 : 26 (Scheme 3).[12] Michael addition of triflinate anion to 3-cyclopentyl-1-propynyl-λ^3-bromane **1c** afforded the bicyclooctene **4b** with high selectivity (>96%).

Formation of both 1-sulfonylcyclopentenes and 1-alkynyl sulfones is indicative of the intermediacy of reactive alkylidene carbenes **6**, produced *via* Michael addition of sulfinate anions and the subsequent elimination of *p*-(trifluoromethyl)bromobenzene, as shown in Scheme 4. Generation of alkylidene carbenes **6** is well established in the reactions of 1-alkynyl(phenyl)-λ^3-iodanes with sulfinate anions.[8,13] An intramolecular 1,5-carbon–hydrogen insertion in alkylidene carbenes **6**, yielding cyclopentenes **2**, is generally preferred over the 1,2-migration of sulfonyl groups which affords 1-alkynyl sulfones **3** because of the low migratory aptitude of sulfonyl groups.

In conclusion, we found that 1-alkynyl(aryl)-λ^3-bromanes serve as efficient Michael acceptors for sulfinate anions and undergo tandem Michael addition–carbene insertion reactions, yielding 1-sulfonylcyclopentenes.

Notes and references

† *Representative procedure* (Table 1, entry 3): to a stirred solution of 1-decynyl-λ^3-bromane **1a** (23 mg, 0.052 mmol) in dichloromethane (2 mL) was added sodium benzenesulfinate (5.7 mg, 0.034 mmol) at 0 °C under argon and the mixture was stirred for 1 h. The mixture was poured into water and extracted with dichloromethane. Drying of the extract with Na_2SO_4 and then concentration *in vacuo* afforded a crude oil, which was purified by preparative TLC (hexane–ethyl acetate 7 : 3) to give a 79 : 21 mixture of **2a** and **3a** (8.3 mg, 86%). **2a**:[8] δ_H (400 MHz, $CDCl_3$) 0.88 (t, *J* 6.6 Hz, 3H), 1.19–1.51 (m, 8H), 1.54–1.67 (m, 1H), 2.14–2.25 (m, 1H), 2.39–2.60 (m, 2H), 2.78–2.90 (m, 1H), 6.71 (br s, 1H), 7.54 (dd, *J* 7.6, 7.3 Hz, 2H), 7.63 (t, *J* 7.3 Hz, 1H), 7.90 (d, *J* 7.6 Hz, 2H). **3a**:[8] δ_H (400 MHz, $CDCl_3$) 0.88 (t, *J* 6.8 Hz, 3H), 1.17–1.37 (m, 10H), 1.55 (quint, *J* 7.3 Hz, 2H), 2.36 (t, *J* 7.2 Hz, 2H), 7.57 (dd, *J* 7.8, 7.3 Hz, 2H), 7.67 (t, *J* 7.3, 1H), 8.01 (d, *J* 7.8 Hz, 2H).

‡ *Selected data*: **4a**: colourless oil; ν_{max}(neat)/cm^{-1} 2930, 1605, 1364, 1220, 1136, 624, 580; δ_H (400 MHz, $CDCl_3$) 0.90 (t, *J* 6.6 Hz, 3H), 1.22–1.59 (m, 8H), 1.72–1.84 (m, 1H), 2.29–2.41 (m, 1H), 2.67–2.86 (m, 2H), 2.93–3.05 (m, 1H), 7.16 (br s, 1H); *m*/*z* (EI) 271 [(M + 1)$^+$, <1%], 201 (25), 153 (9), 137 (34), 131 (41), 107 (30), 95 (73), 81 (100), 71 (49), 67 (74), 55 (72); HRMS calc. for $C_{11}H_{18}O_2F_3S$ [(M + 1)$^+$] 271.0980, found 271.0981. **4b**: colourless oil; ν_{max}(neat)/cm^{-1} 2956, 1608, 1362, 1219, 1134, 1062, 1016, 819, 627, 583; δ_H (400 MHz, $CDCl_3$) 1.38–1.64 (m, 4H), 1.81–1.94 (m, 2H), 2.48 (br d, *J* 15.8 Hz, 1H), 2.91–3.09 (m, 2H), 3.40–3.52 (m, 1H), 7.01 (br s, 1H); *m*/*z* (EI) 240 (M$^+$, 9%), 171 (86), 143 (5), 129 (27), 107 (99), 91 (61), 79 (100), 67 (100); HRMS calc. for $C_9H_{11}O_2F_3S$ (M$^+$) 240.0432, found 240.0429. **5a**: colourless oil; ν_{max}(neat)/cm^{-1} 2930, 2205, 1382, 1224, 1130, 1053, 656, 592; δ_H (400 MHz, $CDCl_3$) 0.89 (t, *J* 6.5 Hz, 3H), 1.22–1.47 (m, 10H), 1.68 (quint, *J* 7.3 Hz, 2H), 2.55 (t, *J* 7.3 Hz, 2H); *m*/*z* (EI) 270 (M$^+$, 1%), 228 (5), 214 (7), 174 (12), 159 (16), 145 (10), 121 (13), 107 (40), 95 (85), 81 (100), 67 (29); HRMS calc. for $C_{11}H_{17}O_2F_3S$ (M$^+$) 270.0901, found 270.0941. **5b**: pale yellow oil; ν_{max}(neat)/cm^{-1} 2957, 2203, 1382, 1224, 1129, 1042, 770, 678, 589; δ_H (400 MHz, $CDCl_3$) 1.21–1.34 (m, 2H), 1.55–1.74 (m, 4H), 1.83–1.94 (m, 2H), 2.20 (sept, *J* 7.2 Hz, 1H), 2.56 (d, *J* 7.2 Hz, 2H); *m*/*z* (EI) 241 [(M + 1)$^+$, 7%], 240 (M$^+$, 1), 212 (4), 199 (6), 172 (38), 143 (8), 105 (13), 91 (34), 79 (57), 69 (52), 67 (100); HRMS calc. for $C_9H_{11}O_2F_3S$ (M$^+$) 240.0432, found 240.0434.

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