Scandium triflate catalyzed unexpected cleavage of C-C bonds in ynones

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Abstract
An unexpected C-C bond cleavage in ynones in the presence of catalytic amounts of $Sc(OTf)_3$ in methanol under microwave irradiation has been discussed. The effect of substituent on the regioselectivity of C-C bond cleavage has carefully been addressed by employing various ynones derivatives. The mechanism has been proposed for the observed regioselectivity.

Keywords: C-C bond cleavage, scandium triflate, ynones, ketones, esters

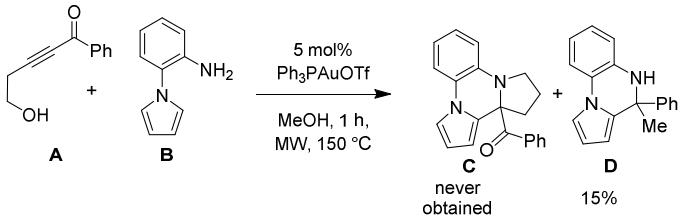
Introduction

The transition-metal-catalyzed selective cleavage of C-C bonds is of fundamental interest and plays a great role in the chemical industry.[1,2] These types of reactions are often unpredictable and in large part originated with serendipitous observations.[3,4] As a result, the development of reactions involving cleavage of C−C bonds is very difficult to realise and pose serious challenge to synthetic organic chemists. Literature scrutiny revealed that significant progress has been made in the field of this research; however, this chemistry has been mainly limited to ring-strained molecules[5-10] and specially designed model compounds.[11,12] Herein, we report $Sc(OTf)_3$ catalysed C-C bond cleavage in ynones that leads to synthesis of ketones that from ynones would have poor atom economy of ketones.

Results and Discussion

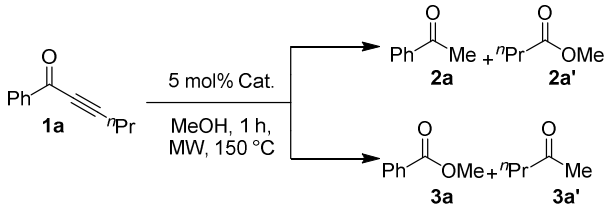
We recently, reported Pt(IV)/Au(I)-catalysed hydroamination-triggered cyclization strategy to

access biologically interesting *N*-containing heterocycles from aminoaromatics and alkynols under conventional heating as well as under microwave assisted conditions.[13-16] During these studies, we had occasion to examine the reaction of δ-hydroxyalkynones **A** with 2-aminophenyl pyrrole **B** in MeOH under microwave conditions (Scheme 1). The formation of polyheterocycle[17] **C** was expected based on the assumption that *endo*-cyclization might favour over to *exo*-cyclization due to the ring strain of incipient methyleneoxetane. The hypothesis was, in part, supported by the assumption that appropriate catalysts may bias the *exo*- and *endo*-cyclization mode. When **A** and **B** reacted under the standard microwave assisted conditions, the product **D** was obtained in 15% yield and none of the expected product **C** was observed. The formation of **D** was very surprizing to us and indicated in situ generation of acetophenone through cleavage of C(sp)-C(sp) bond in **A**. As a natural phenomenon, our efforts were directed to understand mechanistic paths by which acetophenone was generated.



Scheme 1. Unexpected observation in hydroamination-hydroarylation cascade.

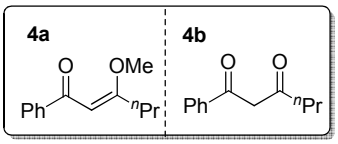
Table 1. Catalysts screening[a]



Entry	Cat.	Yield (%) (**2a**)[b]	Ratio (**2a:3a**)[c]
1	$Ph_3PAuOTf$	20	15:1
2	$Ph_3PAuNTf$	10	14:1
3	$Cu(OTf)_2$	60	18:1
4	$Zn(OTf)_2$	20	20:1
5	$Yb(OTf)_3$	75	22:1
6	$In(OTf)_3$	35	16:1
7	$Sc(OTf)_3$	87	23:1
8	$Bi(OTf)_3$	40	15:1
9	$Sc(OTf)_3$	-[d]	-
10	HCl	91[e,f]	-
11	-	85[g]	-

[a]Reactions were performed in methanol (2 mL) using **1a** (0.58 mmol) and 5 mol% of catalysts at

150 °C for 1 h under microwave irradiation. (Biotage, Initiator Eight, single-mode reactor). [b]Isolated yield. [c]Ratio determined by ^{1}H NMR of a crude mixture. [d]Reaction was performed by conventional heating at 150 °C. [e]0.2 ml (6 N HCl) was used. [f]Product **4b** was obtained. [g]Product **4a** was obtained. Note: Product **2a'** and **3a'** are volatile and therefore were not isolated.



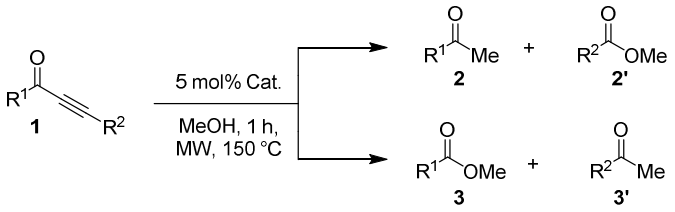
Next, we started our investigation using ynones **1** as the model substrate (Table 1). The 1-phenylhex-2-yn-1-one (**1**) was subjected $Ph_3PAuOTf$ catalysis under the standard conditions, in the absence of **B**. Indeed, the acetophenone was obtained in 20% yield (entry 1). The use of $Ph_3PAuNTf_2$ catalyst also shows somewhat similar results (entry 2). Next, various Lewis acids catalysts such as $Cu(OTf)_2$, $Zn(OTf)_2$, $Yb(OTf)_3$, $In(OTf)_3$, $Sc(OTf)_3$ and $Bi(OTf)_3$ has been investigated (entries 3-8). The best result was obtained with 5 mol% of $Sc(OTf)_3$ in MeOH that afforded **2a**/**3a** in 87% yield with good regioselectivity (23:1) (entry 7). The products of **2a′** and **3a′** were not isolated due to their volatile nature. Similarly, when reaction was carried out under conventional heating at 150 °C in pressure tube, the starting material was remain unreacted (entry 9). Interestingly, when HCl was used in stoichiometric amount, the 1,3-diketone **4b** was obtained as a sole product (entry 10).[18] As can be judged from entries 11 that the only Michael addition product **4a** was obtained in absence of any catalyst.

Encouraged by these findings and with the optimized conditions in hand (Table 1, entry 7), we turned our attention to explore the generality of this reaction and the results of this investigation are summarized in Table 2. The reaction manifests a broad substrate scope as can be judged from entries 1-12 that various substituents in R^1 and R^2 reacts well giving C-C bond cleavage products in good yields (entries 1-12). The halo groups such as bromo, iodo (entries 1 and 2) and electron withdrawing groups (entry 3) on the aryl moiety of carbonyls were tolerated well under the optimized reaction condition with good yields and high regioselectivity. The cinnamyl substituent on the carbonyls also worked well under the standard reaction conditions with high regioselectivity (entry 4). The electron donating groups such as mono and disubstituted methoxy groups on meta-position (entries 5 and 6) and sterically bulkier groups (entry 7) gave higher ratio of **2:3**. In case of symmetrical ynones (entry 10) the product was obtained in good yield with equal ratio of **2:3**. Interestingly, hetero groups on the carbonyls and terminal alkynes gave a single regioisomer (entries 8-9). Even the aliphatic substituent on the terminal acetylene such as ^{n}Hex and cyclopropyl could be smoothly transformed into the desired products with high yields and excellent regioselectivity (entries 11-12). In case of symmetrical ynones only one set of carbon-carbon bond cleavage products (**2a** and **2a'**) are possible. On the other hand, unsymmetrical ynones might give rise upon C-C bond cleavage products in two set of products such as **2a**/**2a'** and **3a**/**3a'**, but experimental result showed only few cases two pair of products

were obtained.

Extensive literature study reveals that there exist quite a few reports catalytic cleavage of C(sp)-C(sp) bonds of unactivated alkynes.[19-24] However, such kind of C(sp)-C(sp) bond cleavage in ynones are remains uncommon[25]. Similarly, it should be noted that the such kind of cleavage in 1,3-diketone[26,27] has literature precedence; however, the use of naked H^+,[28-32] amines[33] or strong bases[34-35] are necessary and the reactions are low yielding.[36] Despite these precedents, the catalytic cleavage of C-C bond in 1,3-diketones has, to date, not evolved into a synthetically useful methodology.

Table 2. Scope with ynones[a]

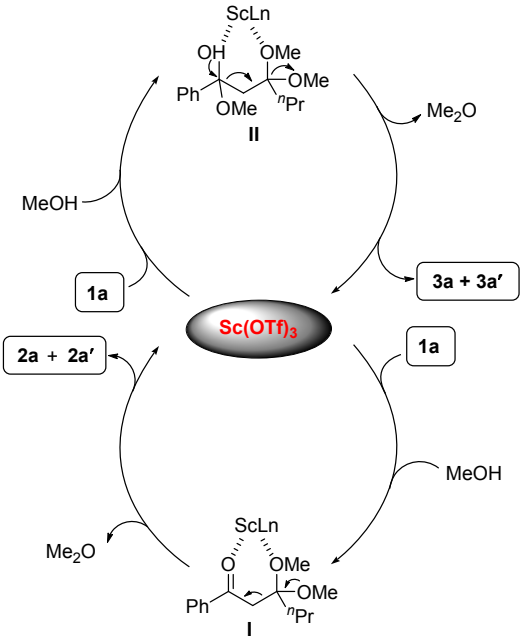


Entry	Substrate			Yield (%)[b]	Yield (%)[b]	Ratio
	1	R^1	R^2	**2**	**3**	(**2:3**)[c]
1	**1b**	4-Br-C_6H_4	^{n}Pr	79	-[d]	8:1
2	**1c**	4-I-C_6H_4	^{n}Pr	40	53[e]	1:1.4
3	**1d**	R^1 = 4-NO_2-C_6H_4	^{n}Pr	65	-[d]	4.2:1
4	**1e**	Cinnamyl	^{n}Pr	83	-[d]	8.1:1
5	**1f**	3-OMe-C_6H_4	^{n}Pr	87	-[d]	9:1
6	**1g**	3,5-OMe-C_6H_3	^{n}Pr	21	71[e]	1:3
7	**1h**	2-Naphthyl	^{n}Pr	81	-[d]	9.6:1
8	**1i**	2-thienyl	^{n}Pr	78	-[d]	1:0
9	**1j**	2-Furyl	^{n}Pr	85	-[d]	1:0
10	**1k**	Ph	Ph	65	30[e]	1.5:1
11	**1l**	Ph	^{n}Hex	67	-[d]	27:1
12	**1m**	Ph	Cyclopropyl	62	35[e]	1.7:1

[a]Reactions were performed in methanol (2 mL) using **1** (0.58 mmol) and 5 mol% of catalysts at 150 °C for 1 h under microwave irradiation. [b]Isolated yield. [c]Ratio was determined by ^{1}H NMR spectrum of a crude mixture. [d]Product was obtained in negligible amount and therefore proved difficult to isolate. [e]Product were formed in significant amount and therefore we could isolate. Note: Product **2'** and **3'** are volatile and therefore we were unable to isolate.

While precise reaction mechanism requires further studies, the plausible mechanism is outlined in Scheme 2. Firstly, the coordination of a ynones **1a** to Scandium would take place which triggers the nucleophilic attack of two methanol molecules on to a triple bond to from

intermediate **I**. The intermediate **I**, as shown by arrows, would undergo carbon-carbon bond cleavage to give acetophenone **2a** and aliphatic ester **2a'** with a regeneration of the metal catalyst. In some cases, the intermediate **II** would be generated due to the addition of methanol on carbonyl group (via intermediate **I**). The resulted intermediate **II** would undergo carbon-carbon bond cleavage to give aromatic ester **3a** and ketones **3a'**.



Scheme 2. The plausible mechanism.

Conclusions

We realized an unexpected $Sc(OTf)_3$ catalysed C-C bond cleavage in ynones under MW irradiation in methanol. The detailed investigation on the electronic/steric effects of the substituent on ynones for obtaining high regioselectivity will be investigated in the future.

Acknowledgements

Generous financial support by the DST-New Delhi (No. SB/S1/OC-17/2013) and CSIR-New Delhi (CSC0108 and CSC0130) is gratefully acknowledged. We also thanks to Indian National Science Academy (INSA) for providing a contingency grants (No. SP/YSP/66/2012) for the period of three years.

Experimental Section

General. Ynones **1a**,[37] **1f**,[38] **1k**,[38] **1l**,[39] and **1m**[40] are literature known compounds. Ynones **1b-j** were not known in the literature and therefore prepared from corresponding benzoyl chlorides (method A) or benzaldehyde (method B) as shown below (Scheme 1 and 2).

Preparation of ynones; Method A. To a solution of the alkyne (2 mmol) and acid chloride (3 mmol) in dry THF (4 ml), under a nitrogen atmosphere, was added $PdCl_2(PPh_3)_2$ (1 mol%) and CuI (3 mol%). After 5 min of stirring, Et_3N (2.5 mmol) was added and the reaction left to stir for 1 hr at RT. During this time Et_3N.HCl precipitated out of the solution and the solution became dark orange/brown in color. The reaction was then diluted with ethyl acetate (30 mL) and washed with H_2O (30 mL). The aqueous layer was then extracted with ethyl acetate (3 × 30 mL) and all organics combined and dried (Na_2SO_4). The suspension was then filtered, concentrated and purified by flash chromatography(silica gel 100-200 mesh) using ethyl acetate and pet ether solvent system.

Method B. To a solution of ^{n}BuLi in hexane (1.32 mL, 1.6 M, 3.3 mmol) terminal alkynes (0.36 mL, 3.3 mmol) in dry THF (6 mL) was added at –78 °C under nitrogen atmosphere. The mixture was stirred for 1 h at –78 °C then benzaldehyde (0.305 mL, 3.0 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h and quenched with a saturated aqueous NH_4Cl solution. The aqueous solution was extracted with ethyl acetate (2 × 15 mL), and the combined organic layers were washed with brine (20 mL). After the organic layer was dried with $NaSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography with hexane/EtOAc to afford propargylic alcohols. Activated MnO_2 (10 equiv.) was added to the solution of propargylic alcohol in DCM (5 mL) and stirred at room temperature for 12 h. Upon completion of reaction, the suspension was filtered through celite and the filtrate was concentrated. The crude product was purified by column chromatography using hexane/EtOAc as eluent to afford ynone.

1-(4-Bromophenyl)hex-2-yn-1-one (1b). Compound **1b** (pale yellow liquid, 78%) was prepared following the general procedure method A; R*f* 0.60 (hexane/EtOAc 90/10); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01-7.97 (m, 2H), 7.63-7.60 (m, 2H), 2.48 (t, *J* 7.01 Hz, 2H), 1.17 (sext, *J* 7.32 Hz, 2H), 1.08 (t, *J* 7.47 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.8, 134.9, 131.0, 130.1, 128.4, 96.4, 78.7, 20.7, 20.3, 12.9; IR (film): ν_{max} 2940, 2932, 2860, 2209, 1663, 1469, 1366, 1167, 735, 701 cm^{-1}; MS (ESI): *m/z* 251 (M^+ + H); HRMS calcd for $C_{12}H_{11}BrO$ (M^+ + H) 251.0066, found 251.0067.

1-(4-Iodophenyl)hex-2-yn-1-one (1c). Compound **1c** (pale yellow thick liquid, 57%) was prepared following the general procedure method A; R*f* 0.50 (hexane/EtOAc 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12-8.01 (m, 1H), 7.70-7.98 (m, 2H), 7.45 -7.65 (m, 1H), 2.45 (t, *J* 7.01 Hz, 2H), 1.55 – 1.80 (m, 2H), 1.10 (t, *J* 7.15 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.1, 137.6, 131.5, 130.5, 102.2, 97.2, 79.3, 21.1, 20.0, 13.4; IR (film): ν_{max} 2960, 2928, 2815, 2201,

1645, 1612, 1425, 1170, 735, 715 cm^{-1}; MS (ESI): *m/z 298* (M^+ + H); HRMS calcd for $C_{12}H_{11}IO$ (M^+ + H) 298.9927, found 298.9924.

1-(4-Nitrophenyl)hex-2-yn-1-one (1d). Compound **1d** (pale yellow liquid, 65%) was prepared following the general procedure method A.; R*f* 0.35 (hexane/EtOAc 90/10); ^1H NMR (500 MHz, $CDCl_3$): δ 8.38-8.24 (m, 4H), 2.53 (t, *J* 7.01, 2H), 1.80-1.69 (m, 2H), 1.10 (t, *J* 7.47 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.9, 150.6, 140.9, 130.3, 128.4, 128.1, 123.6, 99.1, 79.4, 21.2, 21.1, 13.5; IR (neat): ν_{max} 2965, 2935, 2223, 2842, 1665, 1545, 1511, 1385, 1444, 1366, 1167, 739, 701 cm^{-1}; MS (ESI): *m/z* 218 (M^+ + H); HRMS calcd for $C_{12}H_{11}NO_3$ (M^+ + H) 218.0812, found 218.0811.

(*E*)-1-Phenyloct-1-en-4-yn-3-one (1e). Compound **1e** (pale yellow liquid, 86%) was prepared following the general procedure method B; R*f* 0.60 (hexane/EtOAc 90/10); ^1H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* 16.05 Hz, 1H), 7.56 (dd, *J* 2.0, 6.0 Hz, 2H), 7.46-7.38 (m, 3H), 6.77 (d, *J* 16.2 Hz, 1H), 2.45 (t, *J* 7.0 Hz, 2H), 1.75 – 1.60 (m, 2H), 1.08 (t, *J* 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.6, 148.1, 134.0, 128.9, 128.5, 130.9, 133.0, 128.2, 94.9, 79.3, 21.0, 21.3, 13.5.; IR (Film): ν_{max} 2995, 2870, 2215, 1655, 1625, 1433, 715, 701 cm^{-1}; MS (ESI): *m/z* 199 (M^+ + H); HRMS calcd for $C_{14}H_{14}O$ (M^+ + H) 199.1117, found 199.1116.

1-(3,5-Dimethoxyphenyl)hex-2-yn-1-one (1g). Compound **1g** (colorless thick liquid, 71%) was prepared following the general procedure method A; R*f* 0.40 (hexane/EtOAc 90/10); ^1H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* 2.2 Hz, 2H), 6.68 (t, *J* 2.2 Hz, 2H), 3.84 (s, 6H), 2.47 (t, *J* 7.0 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.09 (t, *J* 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.4, 160.5, 138.6, 106.2, 106.8, 96.1, 79.6, 55.3, 55.2, 20.9, 21.1, 13.3; IR (film): ν_{max} 2929, 2920, 2832, 2215, 1631, 1525, 1423, 1347, 1165, 738, 701 cm^{-1}; MS (ESI): *m/z* 233 (M^+ + H); HRMS calcd for $C_{14}H_{16}O_3$ (M^+ + H) 233.1172, found 233.1173.

1-(Naphthalen-2-yl)hex-2-yn-1-one (1h). Compound **1h** (pale yellow liquid, 81%) was prepared following the general procedure method B; R*f* 0.70 (hexane/EtOAc 90/10); ^1H NMR (300 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.14 (dd, *J* 1.6, 8.6 Hz, 1H), 8.00 (d, *J* 7.7 Hz, 1H), 7.88 (d, *J* 8.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.58-7.54 (m, 1H), 2.54 (t, *J* 7.0, Hz, 2H), 1.79-1.17 (m, Hz, 2H), 1.13 (t, *J* 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.0, 135.9, 132.2, 127.7, 123.8, 126.7, 128.2, 128.7, 129.6, 128.1, 128.4, 132.4, 134.3, 96.4, 79.8, 21.1, 21.3, 13.5; IR (neat): ν_{max} 3067, 2921, 2822, 1659, 1628, 1422, 1346, 725, 712 cm^{-1}; MS (ESI): *m/z* 223 (M^+ + H); HRMS calcd for $C_{16}H_{14}O$ (M^+ + H) 223.1117, found 223.1119.

1-(Thiophen-2-yl)hex-2-yn-1-one (1i). Compound **1i** (pale yellow liquid, 68%) was prepared following the general procedure method B; R*f* 0.60 (hexane/EtOAc 90/10); ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* 3.7 Hz, 1H), 7.68 (d, *J* 6.0 Hz, 1H), 7.15 (t, *J* 4.5 Hz, 1H), 2.46 (t, *J* 7.5 Hz, 2H), 1.70 (sext, *J* 7.5 Hz, 2H), 1.08 (t, *J* 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 144.8, 134.8, 128.0, 128.4, 95.1, 79.2, 20.9, 21.1, 13.4; IR (film): ν_{max} 2925, 2928, 2196, 1640, 1622, 1513, 1469, 1132, 728, 711 cm^{-1}; MS (ESI): *m/z* 201 (M^+ + Na); HRMS calcd for $C_{10}H_{10}OS$ (M^+ + H) 179.0525, found 179.0524.

1-(Furan-2-yl)hex-2-yn-1-one (1j). Compound **1j** (pale yellow liquid, 78%) was prepared following the general procedure method B; R*f* 0.60 (hexane/EtOAc 90/10); ^1H NMR (300 MHz,

$CDCl_3$): δ 7.64 (dd, *J* 1.0, 1.5 Hz, 1H), 7.32 (dd, *J* 0.7, 3.5 Hz, 1H), 6.56 (dd, *J* 1.6, 3.5 Hz, 1H), 2.44 (t, *J* 7.0 Hz, 2H), 1.68 (sext, *J* 7.2 Hz, 2H), 1.07 (t, *J* 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3): δ 164.7, 152.9, 147.6, 120.6, 112.3, 95.1, 78.8, 20.7, 21.0, 13.2; IR (film): ν_{max} , 2998, 2865, 2165, 1623, 1435, 1325, 1160, 739, 701 cm^{-1}; MS (ESI): *m/z* 163 (M^+ + H); HRMS calcd for $C_{10}H_{10}O_2$ (M^+ + H) 163.0754, found 163.0753.

General procedure for C-C bond cleavage. A solution of ynones and (0.58 mmol) and $Sc(OTf)_3$ (5 mol%) in MeOH (2 mL) was sealed under nitrogen in reaction vials and irradiated in a microwave reactor (Biotage initiator 8, single-mode reactor) at 150 °C for 1 h. On cooling of the reaction mixture to ambient temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography using hexane/EtOAc as eluent to afford products.

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