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Ruthenium-Catalyzed Transformation of Aryl and Alkynyl Propargyl Ethers into Aryl and Alkynyl Ketones via Cleavage of a Carbon−Carbon Triple Bond

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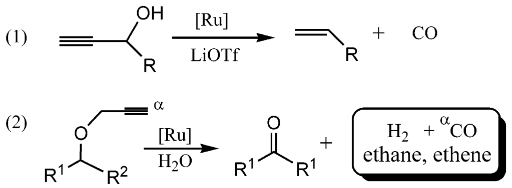
Summary: Treatment of aryl and alkynyl propargyl ethers with water and $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst in hot dichloroethane led to the removal of the propargyl ether group and gave aryl and alkynyl ketones efficiently. Analysis of the gaseous mixture above the reaction solution showed the presence of carbon monoxide, ethylene, ethane, and carbon monoxide, produced from degradation of the propargyl ether functionality with water. A plausible reaction mechanism is proposed on the basis of reaction products. This catalytic reaction proves to be a reliable method to obtain aryl and alkynyl ketones from their propargyl ether derivatives.

Introduction

Metal-catalyzed cleavage of carbon−carbon bonds is a fascinating topic in organic reactions.[1] Cleavage of a carbon−carbon triple bond is difficult, because this functionality generally gives products containing C═C and C−C bonds during catalytic reactions.[1,2] Metal-mediated cleavage of a carbon−carbon triple bond has been extensively studied in stoichiometric organometallic reactions;[3−6] examples include oxidative cleavage of alkyne to carboxylic acids,[3] alkyne cleavage across metal−metal bonds,[4] water-assisted splitting of alkyne into alkane and CO,[5] and alkyne ligand scission on a metal center.[6] Although there is considerable interest to realize this process through a catalytic reaction, successful examples are few. Jun et al. reported catalytic cleavage of alkyne through rhodium-catalyzed hydroiminoacylation.[7] Yamamoto and co-workers reported the cleavage of diynes via ruthenium-catalyzed hydroamination.[8] A similar phenomenon was observed by the same group for the benzannulation of *o*-alkynyl(oxo)benzenes.[9] Recently, we reported the ruthenium-catalyzed transformation of ethynyl alcohol into alkene and carbon monoxide (Scheme 1, eq 1).[10] The reaction mechanism is shown to involve an ruthenium−allenylidenium intermediate according to isotope labeling experiments.[10] As a continuation of this work, we report a new catalytic transformation of alkynyl and aryl propargyl ethers into alkynyl and aryl ketones using the same ruthenium catalyst; this process is considered to be a new pattern of transfer hydrogenation via water-assisted degradation of the propargyl ether functionality into ethene, CO, and H_2. This reaction is mechanistically interesting because the mechanism is proposed to involve cleavage of a carbon−carbon triple bond.

Scheme 1



Results and Discussion

We first examined the effect of solvents and catalysts on catalytic reaction. Treatment of the alkynyl propargyl ether **1a** with $TpRuPPh_3(CH_3CN)_2PF_6$[11] (5.0 mol %) in wet 1,2-dichloroethane (95 °C, 12 h, 2.0 equiv of H_2O) gave alkynyl ketone **2a** in 83% yield (Table 1). Ketone **2a** was obtained in 36% yield in the absence of water. The yield of ketone **2a** was as high as 91% if a high loading (10 mol %) catalyst was used. GC analysis of the gaseous mixture of the reaction solution in a sealed tube (5.0 mol % catalyst) showed the presence of carbon

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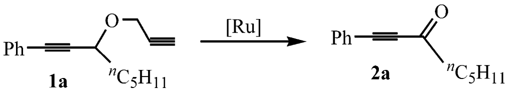
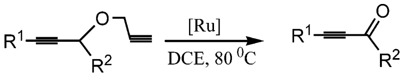
Table 1. Catalytic Transformation over Various Solvents and Catalysts[a]



entry	catalyst	solvent	conditions	yield (%)[b]
1	$TpRuPPh_3(CH_3CN)_2PF_6$	DCE	80 °C, 12 h	83 (91)[c]
2	$TpRuPPh_3(CH_3CN)_2PF_6$	CH_3CN	90 °C, 24 h	24 [50][d]
3	$TpRuPPh_3(CH_3CN)_2PF_6$	DME	85 °C, 72 h	2 [67]
4	$TpRuPPh_3(CH_3CN)_2PF_6$	benzene	80 °C, 72 h	6 [68]
5	$TpRuPPh_3(CH_3CN)_2PF_6$	EA	80 °C, 72 h	trace [54]
6	$TpRuPPh_3(CH_3CN)_2PF_6$	DMF	110 °C, 48 h	34 [25] (51)[c]
7	$TpRuPPh_3(CH_3CN)_2OTf$	DCE	80 °C, 18 h	56
8	$TpRuPPh_3(CH_3CN)Cl$	DCE	80 °C, 18 h	N.R. [70]
9	$CpRuPPh_3(CH_3CN)_2PF_6$	DCE	80 °C, 12 h	N.R. [74]

[a] Conditions: 5.0 mol % catalyst, [substrate] = 0.80 M. [b] Products were isolated from a silica column. [c] The values in parentheses represent isolated yields for 15 mol % catalyst. [d] The values in brackets represents the recovery yields of ether.

Table 2. Catalytic Transformation of Various Alkynyl Propargyl Ethers[a]



entry	ether	ketone (yield (%))[b]
1	$R^1 = Ph$, $R^2 = {}^{n}C_4H_9$ (**1b**)	**2b** (84)
2	$R^1 = {}^{n}C_6H_{13}$, $R^2 = Ph$ (**1c**)	**2c** (79)
3	$R^1 = {}^{t}C_4H_9$, $R^2 = Ph$ (**1d**)	**2d** (82)
4	$R^1 = {}^{n}C_6H_{13}$, $R^2 = Et$ (**1e**)	**2e** (82)
5	$R^1 = {}^{n}C_6H_{13}$, $R^2 = {}^{i}C_3H_7$ (**1f**)	**2f** (82)
6	$R^1 = {}^{n}C_6H_{13}$, $R^2 = {}^{t}C_4H_9$ (**1g**)	**2g** (84)
7	$R^1 = Ph$, $R^2 = H$ (**1h**)	N.R.

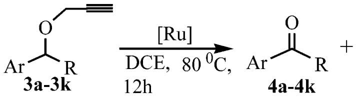
[a] Conditions: 5.0 mol % catalyst, [substrate] = 0.80 M, 12 h, H_2O (1.0 equiv). [b] Products were isolated from a silica column.

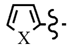
monoxide (53%), ethane (30%), ethane (27%), and hydrogen (31%). Under similar conditions, other solvents were less effective than 1,2-dichloroethane and gave 0−34% yields of alkynyl ketone **2a** (entries 2−6) with recovery of starting ether **1a** in 50%-68% yields. DMF showed a mild activity to give a 51% yield of ketone **2a** with 8 mol % catalyst. We examined three other catalysts to assess the effect of catalyst ligands. A decrease in the yield (56%) of ketone **2a** was observed for $TpRuPPh_3(CH_3CN)_2OTf$.[12] A more strongly ligating chloride as in $TpRuPPh_3(CH_3CN)Cl$[6] led to catalytic inactivity because of a less vacant site. No catalytic activity was seen for $CpRuPPh_3(CH_3CN)_2PF_6$ catalyst.[13]

We prepared various alkynyl propargyl ethers to examine the scope of catalytic reactions. This catalytic reaction is applicable to the replacement of R^1 and R^2 groups of substrates with aryl and alkyl substituents, including phenyl, ethyl, isopropyl, *tert*-butyl, and *n*-hexyl groups; the corresponding ketones **2b**−**g** were obtained in 79−84% yields without formation of byproducts (Table 2). Ether **1h** failed to produce an alkynyl aldehyde product, and 68% of the starting material was recovered.

We examined the suitability of this method for various aryl and heteroaryl propargyl ethers; the results were summarized in Table 3. This catalytic reaction is applicable to derivatives of benzyl propargyl ethers **3a** and **3b**, giving phenyl ketones **4a** and **4b** in respective yields of 90% and 91%. Entries 3−5 show the variation of the para substituent of the phenyl group; the reaction works well with methoxy, fluoro, and trifluoromethyl substituents to give the corresponding ketone derivatives **4c**−**e** in 71−97% yields. As shown in entries 6−8, furanyl, pyrrolyl, and thienyl derivatives **3f**−**h** were equally as active as their phenyl analogues **3a**,**b** in these catalytic reactions. Similarly, the three heteroaryl analogues **3i**−**k** proceeded smoothly with a change of the R^2 group to the 1-octynyl group (entries 9−11).

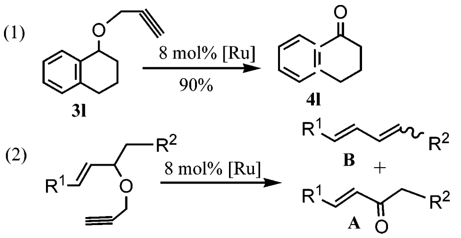
Table 3. Catalytic Transformation of Various Aryl Ethers

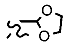


entries	ethers	ketones (yields)[a,b]
1	Ar = Ph, R = ${}^{n}C_4H_9$ (**3a**)	**4a** (90%)
2	Ar = Ph, R = ${}^{n}C_6H_{13}$ (**3b**)	**4b** (91%)
3	Ar = 4-MeOPh, R = ${}^{n}C_5H_{11}$ (**3c**)	**4c** (97%)
4	Ar = 4-FPh, R = ${}^{n}C_5H_{11}$ (**3d**)	**4d** (84%)
5	Ar = 4-CF_3Ph, R = ${}^{n}C_5H_{11}$ (**3e**)	**4e** (71%)
	Ar =  X	
6	X = O, R = ${}^{n}C_6H_{13}$ (**3f**)	**4f** (96%)
7	X = NMe, R = ${}^{n}C_6H_{13}$ (**3g**)	**4g** (80%)
8	X = S, R = ${}^{n}C_6H_{13}$ (**3h**)	**4h** (91%)
9	X = O, R = ▬−${}^{n}C_6H_{13}$ (**3i**)	**4i** (93%)
10	X = NMe, R = ▬−${}^{n}C_6H_{13}$ (**3j**)	**4j** (83%)
11	X = S, R = ▬−${}^{n}C_6H_{13}$ (**3k**)	**4k** (96%)

[a] Conditions: 5.0 mol % catalyst, [substrate] = 0.80 M, 3.0 equiv of H_2O. [b] Products were obtained from a silica column.

Scheme 2



Ether	Products
(a) R^1=Ph, R^2= ${}^{n}C_4H_9$ (**5a**)	**6a(B)** (61%) (E/Z=1.7)
(b) R^1=Ph, R^2=  (**5b**)	**6b(A)** (73%)
(c) R^1=H, R^2=$C_{11}H_{23}$ (**5c**)	**6c(B)** (30%) (E/Z=6.1)

Scheme 2 (eq 1) shows the suitability of this reaction for the cyclic benzyl propargyl ether **3l**, to give the cyclic ketone **4l** in 90% yield**.** We also prepared derivatives of allyl propargyl ethers **5a**−**c**, but only the dioxolane species **5b** produced allyl ketone **6b(A)** in 73% yield, whereas aliphatic substituents **5a** and **5c** followed the elimination reaction to give dienes **6a(B)** and **6c(B)**, respectively. This catalytic process has limited application with respect to derivatives of allyl propargyl ethers.

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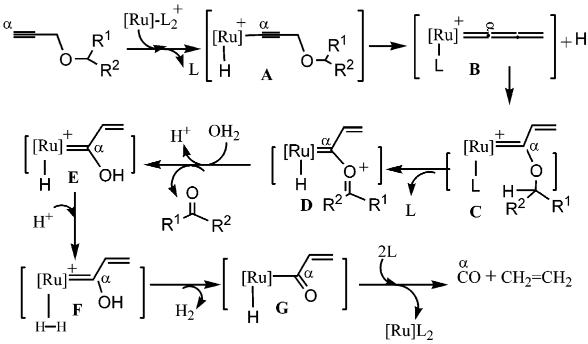
(12) $TpRuPPh_3(CH_3CN)_2OTf$ was prepared from heating an acetonitrile reaction of $TpRu(PPh_3)_2Cl$ with LiOTf according to the procedure described in ref 11.

(13) This catalyst was prepared from treatment of $CpRu(CH_3CN)_3PF_6$ with an equimolar amount of PPh_3.

Scheme 3



Shown in Scheme 3 is a plausible mechanism based on our observation. We found that ethylene, ethane, carbon monoxide, and H_2 in significant proportions were produced with desired ketone products. The reaction likely involves the initial formation of alkynylruthenium hydride species **A** in equilibrium with the ruthenium−allenylidenium species **B**.[10,14] Counterattack of alcohol at species **B** forms the more stable oxacarbenium species **C**. The alkoxy group was activated by the ruthenium center to form the oxonium species **D,** in which the ketone moiety was displaced by water to form ruthenium enol **E** via release of a proton. Reprotonation of this species **D** is expected to give the ruthenium−hydrogen complex **F**, which was subsequently converted to a ruthenium−acyl complex and a free hydrogen. Decarbonylation of species **G** gave ethylene and carbon monoxide.[10] The presence of ethane is likely due to hydrogenation of ethylene with hydrogen over this ruthenium catalyst.[11]

The preceding proposed mechanism involves cleavage of the carbon−carbon triple bond of the propargyl ether functionality. The validity of this mechanism is supported by literature reports.[5,10] The transformation of starting propargyl ether to oxonium species **D** was previously proposed for the conversion of 3-benzyl but-1-ynyl ethers to dienes and benzaldehyde using the same catalyst.[14d] It is also supported by related stoichiometric reactions on water-assisted splitting of alkyne into alkene and carbon monoxide.[5]

In summary, we report the new ruthenium-catalyzed transformation of aryl and alkynyl propargyl ethers into ketone derivatives. The propargyl ether moieties were degraded into carbon monoxide, ethylene, ethane and hydrogen, to leave ketone products alone for easy separation. This reaction is mechanistically interesting because it involves cleavage of a carbon−carbon triple bond. A plausible mechanism is proposed on the basis of our observation and literature reports. This catalytic reaction proves to be a reliable method to obtain aryl and alkynyl ketones from their propargyl ether derivatives.

Experimental Section

(1) General Procedure. Vinylmagnesium bromide, phenylacetylene, propargyl bromide, benzaldehyde, and other aliphatic aldehydes were obtained commercially and used without purification. $TpRu(PPh_3)(CH_3CN)_2PF_6$ was prepared by heating $TpRu(PPh_3)_2Cl$ in CH_3CN according to the literature method.[10] Aryl and alkynyl propargyl ethers were obtained via treatment of the corresponding alcohols with propargyl chlorides in the presence of NaH. Spectral data of compounds **1a−h, 2a−g, 3a−l, 4a−l, 5a−c, 6a(B), 6b(A)**, and **6c(B)** in repetitive experiments are provided in the Supporting Information.

(2) Standard Procedure for the Synthesis of Substrates. Synthesis of (3-(Prop-2-ynyloxy)oct-1-ynyl)benzene (1a). To a dry THF solution (20 mL) of NaH (100 mg, 2.5 mmol) was slowly added 1-phenyloct-1-yn-3-ol (404.6 mg, 2.0 mmol), and the mixture was stirred for 1 h at 0 °C. To this mixture was added 3-bromoprop-1-yne (285.5 mg, 2.4 mmol), and the resulting solution was stirred for 4 h under reflux conditions. The THF was removed under reduced pressure, and the organic layer was extracted with diethyl ether. The solution was dried over $MgSO_4$ and chromatographed (hexane/ether = 10/1, $R_f = 0.51$) over a silica column to give (3-(prop-2-ynyloxy)oct-1-ynyl)benzene (**1a**; 390.4 mg, 1.58 mmol, 79.2%) as a yellow oil.

Procedure for Catalytic Reactions. To a 1,2-dichloroethane solution (1.0 mL) was added propargyl ether **1a** (150 mg, 0.62 mmol), water (13 mg) and $TpRuPPh_3(CH_3CN)_2PF_6$ (38.1 mg, 49.9 μmol), and the reaction mixture was heated at 80 °C for 5 h. The solution was filtered over a short silica bed and then washed with diethyl ether. Concentration of the filtrate under reduced pressure gave 1-phenyl-oct-1-yn-3-one **2a** (89.1 mg, 0.44 mmol, 71.3%) as a yellow oil.

(3) Spectral Data. (3-(Prop-2-ynyloxy)oct-1-ynyl)benzene (1a). IR (Nujol, cm^{-1}): 3296 (m), 3078 (s), 2958 (s), 2210 (m), 1613 (s), 1475 (m), 1263 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 3 H), 7.43 (m, 2 H), 4.49 (t, J = 6.8 Hz, 1 H), 4.35 (ABq, J = 2.4, 15.6 Hz, 2 H), 2.43 (t, J = 2.4 Hz, 1 H), 1.81 (t, J = 7.2 Hz, 2 H), 1.52 (m, 2 H), 1.33 (m, 4 H), 0.89 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7, 128.3, 128.2, 122.5, 87.2, 86.2, 79.6, 74.3, 68.8, 55.7, 35.5, 31.4, 24.9, 22.5, 13.9. HRMS (EI, m/z): calcd for $C_{17}H_{20}O$ 240.1514, found 240.1509.

1-Phenyloct-1-yn-3-one (2a). IR (Nujol, cm^{-1}): 3296 (m), 3078 (s), 2958 (s), 2210 (m), 1723 (s), 1613 (s), 1475 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2 H), 7.40 (m, 3 H), 2.64 (t, J = 7.2 Hz, 2 H), 1.73 (m, 2 H), 1.34 (m, 4 H), 0.89 (t, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.3, 130.6, 133.0, 128.5, 128.2,120.0, 90.5, 87.7, 45.4, 31.1, 23.8, 22.3, 13.8. HRMS (EI, m/z): calcd for $C_{14}H_{16}O$ 200.1201, found 200.1187.

Acknowledgment. We wish to thank the National Science Council of Taiwan for supporting this work.

Supporting Information Available: Spectral data for compounds **1a−h**, **2a−g**, **3a−l**, **4a−l**, **5a−c**, **6a(B)**, **6b(A)**, and **6c(B)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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