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Mercury(II) Triflate-Catalyzed Cycloisomerization of Allenynes to Allenenes

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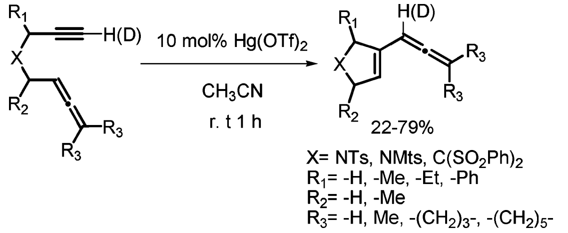
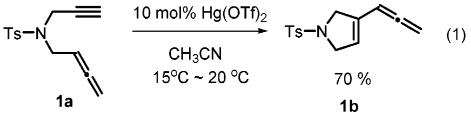


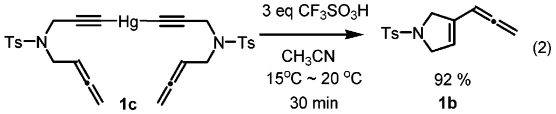
Cycloisomerizations of allenynes to allenenes have been studied in the presence of catalytic amounts of [$Hg(OTf)_2$] in acetonitrile. The catalytic system is quite effective for terminal 1,6-allenynes: allenenes were obtained in reasonable to high yields. However, treatment of allenynes with disubstituents at the allenic terminal carbon yielded a triene and/or allenene as a major product(s) depending upon the substituents.

The transition-metal-catalyzed cyclization of enyne systems has recently experienced tremendous developments.[1] However, Chatani's study[2] on the use of gallium compound as a catalyst in the skeletal rearrangement reaction turned our attention from transition metal catalysts to main group and even lanthanide compounds, such as main group and lanthanide Lewis acids. We recently reported[3] the use of $Au(PPh_3)^+$ or $GaCl_3$ as a catalyst in the cycloisomerization of allenynes to allenenes and initiated studying the use of $Hg(OTf)_2$ as a catalyst in the cycloisomerization. $Hg(OTf)_2$, developed by Nishizawa's group in 1983 as an olefin cyclization agent,[4] now has been developed further into a powerful catalyst for many useful reactions including the hydration of terminal alkynes and the cyclization of enyne, arylyne, and yne-en-aryl substrates.[5] Recently, Echavarren et al. reported[6] the use of $Hg(OTf)_2$ in the cyclization of 1,6-enynes. However, they presented only two examples. We chose allenynes as substrates because they are attractive substrates due to their use in diverse synthetic applications as well as in new reactions of unsaturated systems.[7] Thus, when allenyne **1a** was treated with $Hg(OTf)_2$ in acetonitrile, allenene **1b** was isolated as a major product in 70% yield (eq 1).



Formation of **1b** was also confirmed by an X-ray diffraction study (Figure 1). This was the first observation on a mercury-catalyzed cycloisomerization of allenyne. Encouraged by this result, we initially screened various metal catalysts such as $Hg(CN)_2$, $HgCl_2$, $Hg(OAc)_2$, and $Hg(OTf)_2$ with/without tetramethylurea (TMU), $Cu(OTf)_2$, $Yb(OTf)_3$, and $Sc(OTf)_3$ for the cycloisomerization of allenynes. Results are summarized in Table 1.

Neither $Hg(CN)_2$ nor $HgCl_2$ had any catalytic activity. When $Hg(OAc)_2$ was used as a catalyst, a dimeric product **1c** was obtained in 20% yield with recovery of 40% of the reactant. Formation of **1c** was confirmed by ^1H and ^{13}C NMR and high-resolution mass spectroscopy. Treatment of **1c** with trifluoromethanesulfonic acid in acetonitrile at 15−20 °C for 30 min gave **1b** in 92% yield (eq 2).



When 10 mol % of $Hg(OTf)_2$ was used as a catalyst, the reaction time was shortened to 1 h and the expected product **1b** was obtained in 70% yield. However, when we lowered the catalyst loading to 5 mol %, product **1b** was obtained 38% yield. The catalytic activity in acetonitrile solvent was better than that in THF (77% of the reactant recovered) or dichloromethane (33%

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(1) For reviews, see: (a) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127−2198. (b) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523−596. (c) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635−662. (d) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92.

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10.1021/jo701591e CCC: $37.00

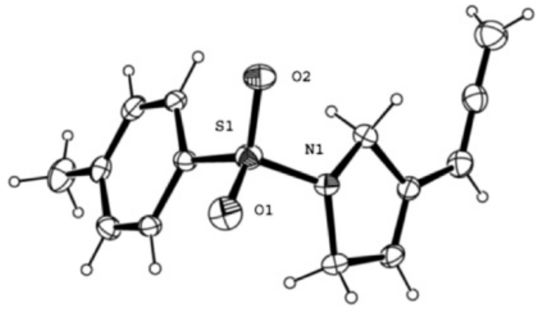
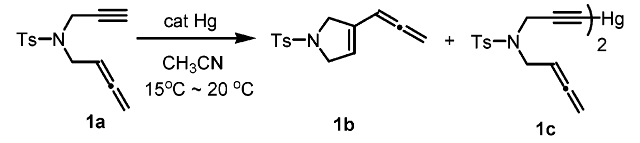


FIGURE 1. X-ray structure of **1b** (30% thermal ellipsoid).

TABLE 1. Hg-Catalyzed Cycloisomerization of Allenynes to Allenenes[a]



entry	catalyst	solvent	*T* (h)	yield[b] (%)
1	10 mol % $Hg(CN)_2$	CH_3CN	24	*c*
2	10 mol % $HgCl_2$	CH_3CN	24	73(**1a**)/(trace)(**1c**)
3	10 mol % $Hg(OAc)_2$	CH_3CN	24	40(**1a**)/20(**1c**)
4	10 mol % $Hg(OTf)_2$	CH_3CN	1	70(**1b**)
5	5 mol % $Hg(OTf)_2$	CH_3CN	24	38(**1b**)
6	10 mol % $Hg(OTf)_2$	THF	24	77(**1a**)
7	10 mol % $Hg(OTf)_2$	CH_2Cl_2	24	33(**1b**)
8	10 mol % $Hg(OTf)_2$ + 20 mol % TMU[d]	CH_3CN	18	38(**1a**)/18(**1b**)/18(**1c**)
9	20 mol % Tf_2O	CH_3CN	24	*c*
10	10 mol % $Cu(OTf)_2$	CH_3CN	24	80(**1a**)/8(**1b**)
11	10 mol % $M(OTf)_3$ (M = Yb, Sc)	CH_3CN	24	*c*

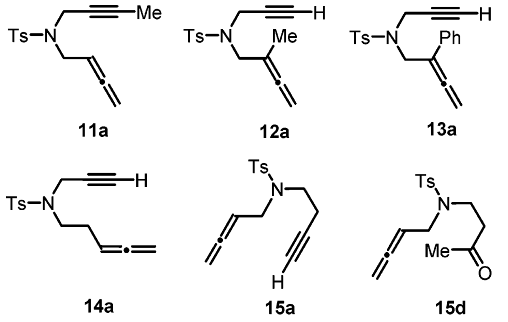
[a] **1a** (0.4 mmol) in 2 mL of CH_3CN was added dropwise to the 1 mL solution of 10 mol % of $Hg(OTf)_2$. [b] Isolated yield. [c] No reaction. [d] TMU = tetramethylurea.

yield for **1b**). Recently, Nishizawa[8] reported that the $Hg(OTf)_2$–TMU complex showed effective catalytic activity for the hydration of terminal alkynes and cyclization. Thus, we used the $Hg(OTf)_2$/TMU system as a catalyst. After 18 h of reaction time, a mixture of **1b** and **1c** (18 and 18%, respectively) was obtained with a recovery of the reactant (38%). When $Cu(OTf)_2$ was used as a catalyst, only 8% of **1b** was isolated with 80% recovery of the reactant. Strangely, no noticeable increase in the yield was found, although 1 equiv of $Cu(OTf)_2$ was used. Disappointingly, neither $Yb(OTf)_3$ nor $Sc(OTf)_3$ was active as a catalyst. Thus, the cycloisomerization of **1a** to **1b** was unique to $Hg(OTf)_2$.

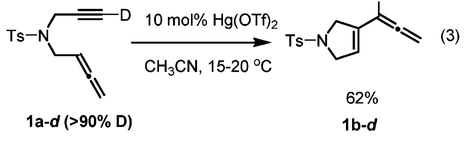
With this result in mind, we screened other allenynes in the presence of a catalytic amount of $Hg(OTf)_2$ in acetonitrile. The results are summarized in Table 2. The reactivity of $Hg(OTf)_2$ was slightly dependent upon the freshness of $Hg(OTf)_2$. However, most of the reactions went to completion within 2 h. Terminal allenynes (entries 1–3) were found to serve as good substrate. This is quite similar to the results of $GaCl_3$- and Au(I)-catalyzed reactions.[3] However, it is in sharp contrast to previously reported results of the Mo-catalyzed RCM of allenynes,[9] where no reaction occurred with allenynes bearing the allenic terminus unsubstituted. Allenynes **4a**–**6a** having a substituent on the 3 position (entries 4 and 5) or having a substituent on the 5 position (entry 6) were also good substrates. Treatment of an allenyne (**7a**) bearing a monosubstituent at the allenic terminal carbon resulted in **7b** in 48% yield. Interestingly, allenynes with disubstituents at the allenic terminal carbon showed a different reaction behavior depending upon the substituents. Allenyne **8a** (entry 7) afforded a mixture of **8b** and **8d** in 34 and 26% yields, respectively. Reaction of allenyne **9a** bearing a cyclic butyl group gave only **9b** as the sole product, although the yield was low (22%). However, treatment of allenyne **10a** with a cyclohexyl group afforded **10d** as the sole product in 46% yield.[10]

Unfortunately, reactions of the substrates shown in Scheme 1 gave no reaction products under the conditions described here. Interestingly, hydration of alkyne **15d** was observed in the reaction of **15a**, although the yield was quite poor (8%).

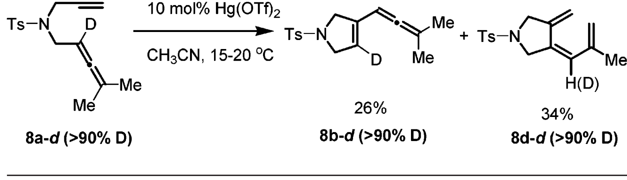
SCHEME 1. Unreactive Substrates for $Hg(OTf)_2$-Catalyzed Cycloisomerization of Allenynes



When allenyne **1a**-*d* with the alkyne terminus deuterated was used, the deuterium was labeled at the 1 position of the produced allenene (eq 3). The same deuterated reaction product was also observed in the $GaCl_3$-catalyzed cycloisomerization of allenynes. When allenyne **8a**-*d* with the deuterated allenene was used, a mixture of the deuterated allenene **8b**-*d* and triene **8d**-*d* was obtained (eq 4).



(3)



(4)

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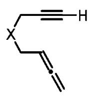
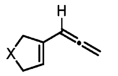
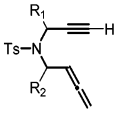
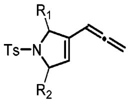
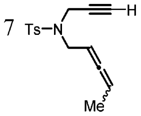
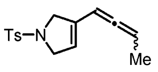
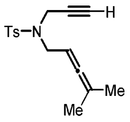
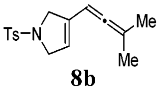
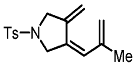
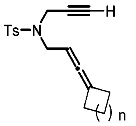
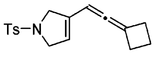
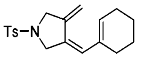
[8] (a) Ménard, D.; Vidal, A.; Barthomeuf, C.; Lebreton, J.; Gosselin, P. *Synlett* **2006**, 57–60. (b) Imagawa, H.; Fujikawa, Y.; Tsuchihiro, A.; Kinoshita, A.; Yoshinaga, T.; Takao, H.; Nishizawa, M. *Synlett* **2006**, 639–641. (c) Nishizawa, M.; Takao, H.; Yadav, V. K.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2003**, *5*, 4563–4565. (d) Nishizawa, M.; Skwarczynski, M.; Imagawa, H.; Sugihara, T. *Chem. Lett.* **2002**, 12–13. (e) Nishizawa, M.; Yadav, V. K.; Skwarczynski, M.; Takao, H.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2003**, *5*, 1609–1611.

[9] Murakami, M.; Kadowaki, S.; Matsuda, T. *Org. Lett.* **2005**, *7*, 3953–3956.

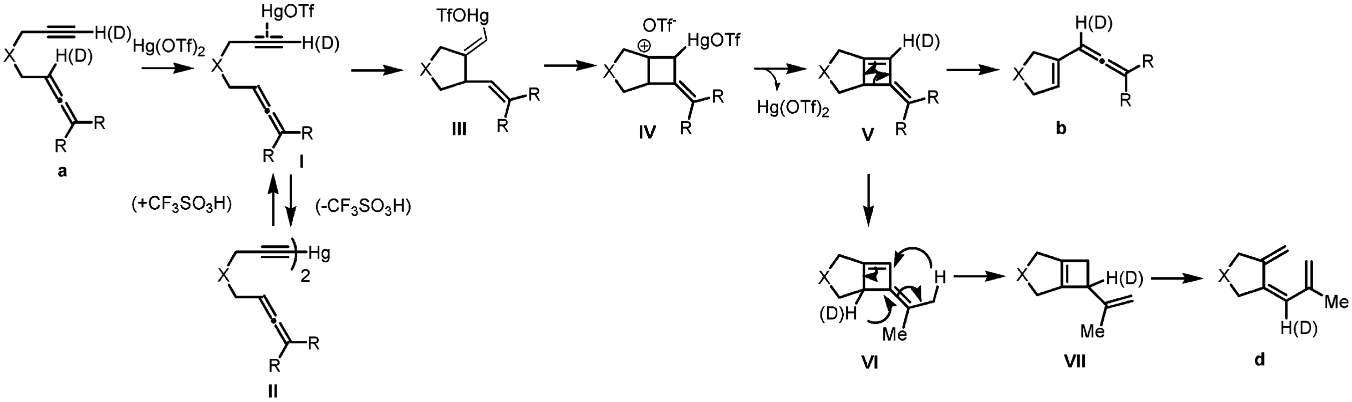
[10] The migrations of H on the allenic substituents were also observed in other literature. See: Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Synlett* **2006**, 575–578.

TABLE 2. $Hg(OTf)_2$-Catalyzed Cycloisomerization of Allenynes to Allenenes[a]

entry	reactant		product	time	yield[b] (%)
1		**1a** (X= NTs)		1 h	62(**1a**)
2		**2a** (X= NMts)		1 h	68(**2b**)
3		**3a** (X= $C(SO_2Ph)_2$)		1 h	79(**3b**)
4		**4a** (R_1= Me, R_2= H)		30 min	62(**4b**)
5		**5a** (R_1= Et, R_2= H)		30 min	59(**5b**)
6		**6a** (R_1= H, R_2= Me)		30 min	72(**6b**)
7		**7a**	 **7b**	2 h	48(**7b**)
8		**8a**  **8b**	 **8d**	1 h	60 (26(**8b**)/34(**8d**))
8		**9a** (n=1) 	**9b**	1 h	22(**9b**)
9		**10a** (n=3) 	**10d**	1 h	46(**10d**)

[a] Allenyne (0.4 mmol) in 2 mL of CH_3CN was added dropwise to the 1 mL solution of 10 mol % of $Hg(OTf)_2$. [b] Isolated yield.

SCHEME 2. Proposed Mechanism for Hg-Catalyzed Cycloisomerization of Allenynes



A general mechanistic view has so far remained elusive. However, on the basis of our experimental observations and the previous studies,[2c,3,11] a plausible reaction mechanism is shown in Scheme 2. A π-complexation of $Hg(OTf)_2$ with alkyne generates **I** as a major intermediate and **II** as a minor intermediate. The intermediate **II** was transformed into **I** in the presence of generated HOTf. Vinylmercuration (**III**) followed by demercuration provides **V**, eventually leading to the generation of **b**. When a substituent on the allenic terminal carbon has protons which can be easily deprotonated, the reaction path will follow the other pathway to the intermediates **VI** and **VII**, and finally to **d**.

In summary, $Hg(OTf)_2$ is also an efficient catalyst for the cycloisomerization of allenynes. The catalytic system is quite effective for terminal 1,6-allenynes: allenenes were obtained in reasonable to high yields. However, for allenynes with disubstituents at the allenic terminal carbon, two mechanistic pathways (to triene vs allenene) operate and the pathway is dependent upon the substituents.

Experimental Section

General Procedure for $Hg(OTf)_2$-Catalyzed Cycloisomerization of Allenynes. A solution of $Hg(OTf)_2$ in CH_3CN (0.04 M, 1 mL) was transferred to a flame-dried 10 mL Schlenk flask. To the flask was added slowly a solution of allenyne (0.4 mmol) in 1 mL of CH_3CN. The reaction mixture was stirred for 1 h. The reaction mixture was quenched by the addition of an aqueous NaCl−$NaHCO_3$ solution. The organic layer was extracted with Et_2O, dried over anhydrous $MgSO_4$, and concentrated. Flash column chromatography on a silica gel column using hexane and EtOAc gave the product.

1c: ^1H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 6H), 3.91 (m, 4H), 4.16 (s, 4H), 4.80 (m, 4H), 5.06 (m, 2H), 7.29 (d, J = 8.0 Hz, 4H),

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[11] (a) Soriano, E.; Marco-Contelles, J. *J. Org. Chem.* **2005**, *70*, 9345−9353. (b) Bruneau, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2328−2334. (c) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704−3709.

7.73 (d, $J = 8.0$ Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 36.5, 45.9, 76.8, 85.6, 99.1, 116.3, 128.2, 129.6, 136.6, 143.7, 209.9 ppm. Exact mass for $C_{28}H_{28}Hg_1N_2S_2O_4$ (FAB+): calcd 723.1276, found 723.1287.

8a-*d*: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.66 (s, 6H), 2.00 (t, $J = 2.3$ Hz, 1H), 2.41 (s, 3H), 3.79 (s, 2H), 4.15 (d, $J = 2.3$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.4, 21.7, 35.7, 46.7, 73.6, 76.7, 97.3, 127.8, 129.6, 136.3, 143.6, 204.1 ppm. Exact mass for $C_{16}H_{18}D_1N_1S_1O_2$ (EI): calcd 290.1199, found 290.1195.

8d: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.75 (s, 3H), 2.42 (s, 3H), 3.80 (d, $J = 3.6$ Hz, 2H), 3.84 (s, 2H), 4.70 (s, 1H), 4.95 (s, 1H), 5.01 (m, 2H), 5.51 (m, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 22.9, 45.7, 49.7, 113.8, 115.5, 121.2, 128.1, 129.8, 133.8, 135.8, 140.8, 143.0, 143.8 ppm. Exact mass for $C_{16}H_{19}N_1S_1O_2$ (EI): calcd 289.1136, found 289.1136.

12a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.71 (m, 3H), 1.96 (t, $J = 2.4$ Hz, 1H), 2.42 (s, 3H), 3.78 (m, 2H), 4.11 (d, $J = 2.4$ Hz, 2H), 4.68 (m, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.0, 21.8, 35.8, 50.1, 73.8, 75.4, 76.8, 93.5, 128.0, 129.7, 136.2, 143.7, 207.8 ppm. Exact mass for $C_{15}H_{17}N_1S_1O_2$ (EI): calcd 275.0980, found 275.0980.

13a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.93 (m, 1H), 2.44 (s, 3H), 4.01(m, 2H), 4.30 (s, 2H), 5.13 (s, 2H), 7.24−7.37 (m, 5H), 7.52 (m, 2H), 7.77 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 35.8, 47.0, 74.3, 76.1, 79.2, 99.8, 126.6, 127.6, 128.2, 128.8, 129.7, 133.3, 135.5, 143.9, 210.2 ppm. Exact mass for $C_{20}H_{19}N_1S_1O_2$ (EI): calcd 337.1136, found 337.1137.

15d: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.09 (s, 3H), 2.36 (s, 3H), 2.77 (m, 2H), 3.29 (m, 2H), 3.76 (m, 2H), 4.64 (m, 2H), 4.83 (m, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 30.3, 42.2, 43.5, 47.9, 76.5, 86.0, 127.3, 129.8, 136.4, 143.5, 207.0, 209.4 ppm. Exact mass for $C_{15}H_{19}N_1S_1O_3$ (HRFAB): calcd 294.1164, found 294.1166. IR (cm^{-1}) 2256 (m), 1705 (s), 1632 (br), 1459 (m).

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Supporting Information Available: Detailed experimental procedures, new characterization data, ^{1}H and ^{13}C NMR spectra of all compounds, and crystallographic data (CIF) of **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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