Ruthenium-catalyzed Hydrative Dimerization of Allenes

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(Received January 25, 2005; CL-050117)

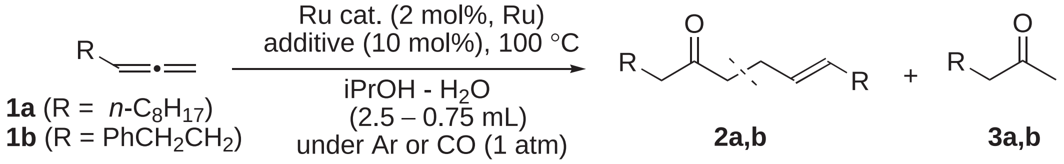
Hydrative dimerization and hydration of allenes proceeded in the presence of a ruthenium catalyst and a strong acid such as trifluoroacetic acid. γ,δ-Unsaturated ketones and methyl ketones were isolated in moderate combined yields. No isomeric compound (isomeric enone) was isolated.

Ruthenium complexes are useful catalysts for the hydration of various unsaturated hydrocarbons.[1] Recent studies revealed that the highly selective hydration of alkynes,[2,3] dienes,[4] and other unsaturated hydrocarbons[5] occurred in the presence of an appropriate ruthenium catalyst. On the other hand, the ruthenium-catalyzed hydration of allenes (1,2-dienes) has not been well explored.

Our interest in the hydration reactions of unsaturated hydrocarbons led us to study the hydration of allenes in the presence of various ruthenium catalysts. In this paper we report the ruthenium-catalyzed hydrative dimerization and hydration of allenes.

The results of the reaction of 1,2-undecadiene (**1a**)[6] and phenethylallene (**1b**)[6] in the presence of ruthenium catalysts are summarized in Table 1. The initial screening of the ruthenium complexes revealed that the hydrative dimerization of **1a** proceeded slowly in the presence of $CpRuCl(PPh_3)_2$[7a] and CF_3COOH (Entry 1). It was important to add both the ruthenium complex and CF_3COOH, otherwise the reaction did not proceed (Entries 2, 3). A bidentate Ru catalyst, CpRuCl(dppm),[7b] was not effective (Entry 4). Among the Ru catalysts[8] we examined, $Ru_3(CO)_{12}$ was most effective, and the dimeric γ,δ-unsaturated ketone **2b** (41%) and the monomeric ketone **3b** (18%) were isolated (Entry 5).[9] It is noteworthy that no isomeric enone other than **2b** was isolated. The best yield of **2** was observed when 10 mol % of CF_3COOH was used (Entries 5–7). Though the yields of the products did not change significantly when the reaction was carried out under CO instead of Ar (Entry 8), the formation of some by-products was suppressed and the isolation of the products was easier.[10] The reaction proceeded rapidly at an elevated temperature (120 °C) but the yield of **2b** decreased (Entry 9). The effect of the acids on this reaction was also investigated, and CF_3COOH turned out to be the best additive: the yields of the products were much lower when the reaction was carried out in the presence of other acids such as CH_3COOH, *p*-TsOH, or HCl, or in the absence of acid (Entries 8–13).[11] We also examined the effects of the solvent on this reaction and carried out the reaction in *t*BuOH–H_2O, EtOH–H_2O, THF–H_2O, CH_3CN–H_2O. However, the yields of the products decreased significantly.

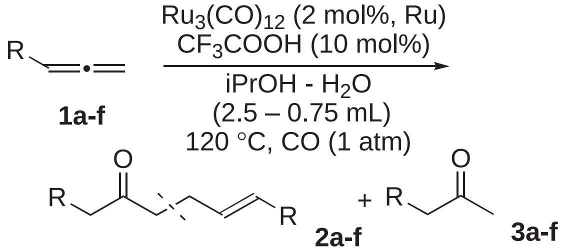
Table 1. Ruthenium-catalyzed hydrative dimerization and hydration of **1a** and **1b**



Entry	Substrate	Catalyst	Additive	Gas	Time/h	Yield of **2**/%[a]	Yield of **3**/%[a]
1	**1a**	$CpRuCl(PPh_3)_2$	CF_3COOH	Ar	18	26	0
2	**1a**	$CpRuCl(PPh_3)_2$	—	Ar	82	0	0
3	**1a**	—	CF_3COOH	Ar	63	0	0
4	**1a**	CpRuCl(dppm)[b]	CF_3COOH	Ar	18	0	0
5	**1b**	$Ru_3(CO)_{12}$	CF_3COOH	Ar	18	41	18
6	**1b**	$Ru_3(CO)_{12}$	CF_3COOH[c]	Ar	18	24	15
7	**1b**	$Ru_3(CO)_{12}$	CF_3COOH[d]	Ar	18	18[e]	8[e]
8	**1b**	$Ru_3(CO)_{12}$	CF_3COOH	CO	18	40	22
9	**1b**	$Ru_3(CO)_{12}$	CF_3COOH	CO	3[f]	33	21
10	**1b**	$Ru_3(CO)_{12}$	CH_3COOH	Ar	18	0	10
11	**1b**	$Ru_3(CO)_{12}$	*p*-TsOH	Ar	17	15	18
12	**1b**	$Ru_3(CO)_{12}$	HCl[g]	CO	24	24	13
13	**1b**	$Ru_3(CO)_{12}$	—	CO	24	—	≈11[h]

[a]Isolated yields. [b]dppm = $Ph_2PCH_2PPh_2$. [c]The reaction was carried out in the presence of 5 mol % CF_3COOH. [d]The reaction was carried out in the presence of 20 mol % CF_3COOH. [e]Yields were determined by NMR. [f]The reaction was carried out at 120 °C. [g]Conc. HCl aq was added. [h]The product was contaminated with a small amount of other by-products.

Table 2. $Ru_3(CO)_{12}$–CF_3COOH-catalyzed hydrative dimerization and hydration of allenes



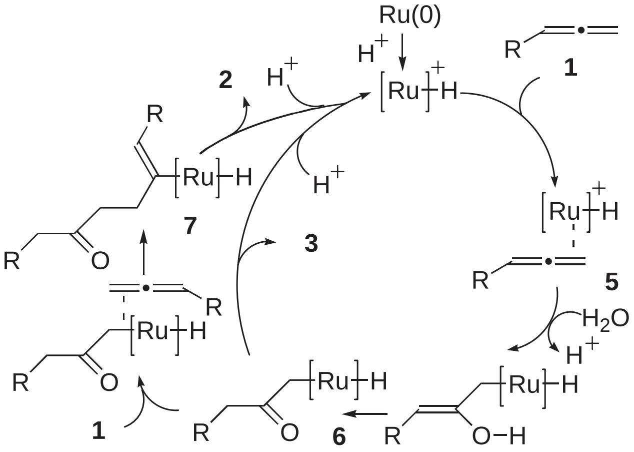
Entry	R	Time /h	Yield of **2** /%	Yield of **3** /%
1	*n*-C_8H_{17} (**1a**)	18[a]	40	22
2	$PhCH_2CH_2$ (**1b**)	3	38	19
3	*n*-C_6H_{13} (**1c**)	3	39	10
4	*n*-$C_{10}H_{21}$ (**1d**)	6	31	18
5	$NCCH_2CH_2$ (**1e**)	7	27	25
6	Cyclohexyl (**1f**)	12	17	8

[a] The reaction was carried out at 100 °C.

The generality of the reaction was examined and the results of the reaction of various allenes were summarized in Table 2. While the reactions of primary alkylallenes, including a cyanoallene, proceeded smoothly and the dimerized products were isolated in 27–40% yields (Entries 1–5), the yield of **2** significantly dropped when cyclohexylallene (**1f**) was used as the substrate (Entry 6). Though we carried out the reaction of other allenes such as phenylallene, phenoxyallene, and ethoxycarbonylallene as well as disubstituted allenes, the corresponding dimer was not isolated.

Since it was not clear whether **2** was formed by the reaction of 2 molecules of **1** with a molecule of water, or by the reaction of **1** with **3**, we examined the reaction of **1b** in the presence of 2-octanone (**4**). The analysis of the products revealed that **2b** was the only dimeric compound which was isolated from the reaction mixture, and **4** was not incorporated. Therefore, it is clear that **2** was not formed by the reaction of **3** with **1**.

The mechanism of this reaction was tentatively assumed as shown in Scheme 1. Thus, the allene would react with a cationic Ru species, formed by the protonation of the $Ru_3(CO)_{12}$, to give a cationic Ru-allene complex **5**. The addition of water to **5** would yield a ketone derivative **6**. A dimeric complex **7** would be formed when allene **1** further reacted with **6**. Protonolysis of **6** and **7** would lead to the formation of **3** and **2**, respectively.[12] Alternatively, the formation of **2** might proceed via the formation and acid-catalyzed hydrolysis of a ruthenacyclopentane.[13] We favor the mechanism proposed in Scheme 1, since the formation of **3** as well as **2** could be reasonably explained.



Scheme 1. Proposed mechanism for the hydrative dimerization and hydration of **1** catalyzed by Ru(0)/acid.

In summary, we found a new ruthenium-catalyzed hydrative dimerization of allenes. The combination of the ruthenium catalyst and a strong acid turned out to be very important for the progress of the reaction. Further elaboration of this reaction is underway.

References and Notes

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8 Though we carried out this reaction in the presence of $Mo(CO)_6$, $RuCl_3$, $Ru_2(CO)_4(C_5H_5)_2$, $RuCl(CO)_2(C_5H_5)$, $[RuCl_2(C_6H_6))]_2$, or Ru(cod)(cot), compound **2** was not isolated and a small amount of **3** (0–21%) was obtained.

9 The formation of non-polar compounds such as 1,3-undecadiene was observed as the by-products. The analysis of the GC-MS spectra indicated the formation of dimeric hydrocarbons.

10 CO may act as a ligand and prevent the decomposition of the catalyst.

11 The formation of **3** in the absence of acid (Entry 13) may be explained in terms of the formation of a small amount of formic acid by the hydration of CO in the reaction mixture.

12 The incorporation of deuterium to the olefinic moiety (52% *d*) (and ketone α-hydrogens, 41% *d*) of **3** was observed when the reaction was carried out in 2-propanol-d_8-D_2O.

13 Five-membered ruthenacycles are postulated as intermediates for various ruthenium-catalyzed reactions. See, Ref 1.

Published on the web (Advance View) March 5, 2005; DOI 10.1246/cl.2005.504