Catalytic Addition of Aromatic C-H Bonds to Acetylenes

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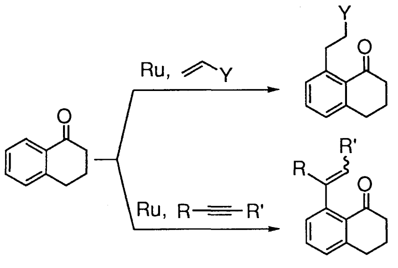
The reaction of α-tetralone with various internal acetylenes can be catalyzed by $Ru(H)_2(CO)(PPh_3)_3$ and gives 1:1 addition products. Symmetrically substituted dialkyl- and diarylacetylenes gave an *E*/*Z* mixture of 1:1 coupling products in good yields. 1-Phenyl-1-butyne afforded all four possible regio- and stereoisomers. 1-Trimethylsilyl-1-propyne gave only *E*-isomer with C-C bond formation exclusively at the carbon atom substituted with the silyl group. Other internal acetylenes having a trimethylsilyl group also proceeded regioselectively although mixtures of stereoisomers were obtained.

We have reported recently that $Ru(H)_2(CO)(PPh_3)_3$ can bring about catalytic addition of C-H bonds at the ortho position of aromatic ketones to olefins (eq 1).[1-3] These catalytic reactions are entirely new and promising as a practical synthetic tool. The catalytic reaction is also applicable to enone/olefin coupling.[4] In the efforts to extend further the scope of the new reaction, we have examined the possibility of replacing the olefins in eq 1 with acetylenes as the acceptor of the C-H bonds (eq 2).[5]



(1)
(2)

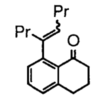
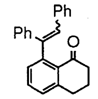
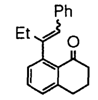
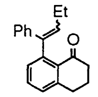
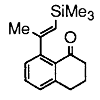
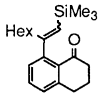
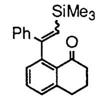
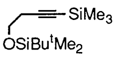
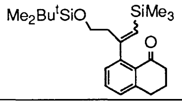
Acetylenes have been known to react with transition-metal complexes in various ways. Terminal acetylenes undergo oxidative addition by their C-H bonds[6] or form vinylidene complex with migration of hydrogen.[7] Via acetylene π complexes, formation of metalacyclopentadiene[8] and trimerization of acetylenes[9] are also known. It was interesting to see whether the desired reaction (eq 2) competes successfully over these known reactions.[6-10]

To begin with we examined the reaction of phenylacetylene with acetophenone (and with other aromatic ketones as well) using $Ru(H)_2(CO)(PPh_3)_3$[11] as the catalyst under various reaction conditions including those that will be described later. No reaction took place. Other terminal acetylenes such as trimethylsilylacetylene, 1-hexyne, and methyl propiolate did not react at all. This was not unexpected since many reaction courses, undesirable for present our purpose, of terminal acetylenes have been reported.[6-10]

We were pleased to see that internal acetylenes did participate in the reaction of eq 2, even though the internal acetylenes are rather sterically crowded. This contrasts to the case of the reaction 1 where internal olefins did not react or reacted only sluggishly.[3] Since α-tetralone (**1**) was the most reactive aromatic ketone in reaction 1,[1-3] substituted acetylenes were subjected to the catalytic reaction using **1**. A typical reaction was carried out by heating **1** (2 mmol), an internal acetylene (4 mmol), and the catalyst $Ru(H)_2(CO)(PPh_3)_3$ (0.12 mmol) in 3 cm^3 of toluene under vigorous reflux (bath temperature was 135 °C). The selected examples of the results of catalytic addition of the C-H bond in α-tetralone to acetylenes are give in Table 1.[12]

Symmetrically substituted dialkyl- (run 1) and diarylacetylenes (run 2) gave 1:1 coupling products in good yields. The addition was highly *cis* selective The reactivity of diphenylacetylene was the highest among those examined so far and one third (i.e., 0.04 mmol) of the catalyst was enough in this case (run 2). In contrast, the yield in run 1 decreased to 48% with the smaller amount of catalyst. All four possible regio- and stereoisomers were formed from an alkylarylacetylene (run 3).

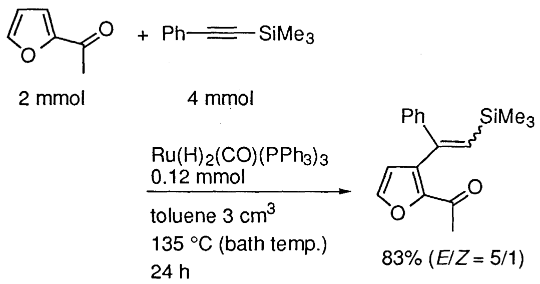
Table 1. Addition of α-Tetralone (**1**) to Acetylenes Catalyzed by $Ru(H)_2(CO)(PPh_3)_3$[a]

Run	Acetylene	Time/h	Product	Yield[b]/%
1	Pr—≡—Pr	4		72% (*E*/*Z* = 16/1)
2[c]	Ph—≡—Ph	1		85% (9/1)[d]
3	Et—≡—Ph	4		73% (5/1)[d]
				27% (5/1)
4	Me—≡—SiMe₃	3		83% (only *E*-isomer)
5	Hex—≡—SiMe₃	2		quantitative (*E*/*Z* = 11/1)
6	Ph—≡—SiMe₃	1		76% (*E*/*Z* = 2/1)
7		21		55% (*E*/*Z* = 11/1)

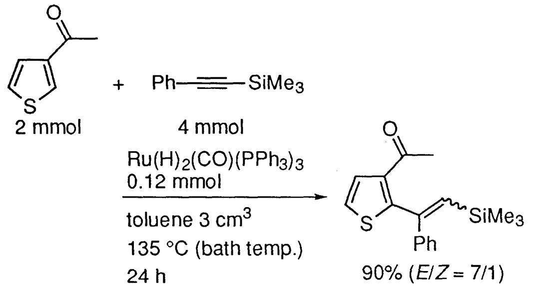
[a]Reaction conditions: **1** (2 mmol), acetylene (4 mmol), $Ru(H)_2(CO)(PPh_3)_3$ (0.12 mmol), toluene (3 cm^3), 135 °C (oil bath tempereature). [b]Isolated yield. [c]Catalyst: 0.04 mmol. [d]The stereochemistry could not be determined.

In contrast, virtually complete regio- and stereoselections were attained when 1-trimethylsilyl-1-propyne was used as the acetylene. Only the *E*-isomer was formed in 83% yield with the regiochemistry shown in run 4 of Table 1. In the case of other trimethylsilylacetylenes, the regioselectivities were exclusive (runs 5-7) although mixtures of stereoisomers were obtained.

Substituted vinylsilanes are known to be highly versatile synthetic bulding blocks.[13] The present catalytic reaction (e.g., runs 4-7) provides an entirely new entry to vinylsilanes, i.e., addition of C-H bonds to silylacetylenes and seems promising as a synthetic reaction. Further examples, shown in eqs 3 and 4 illustrate that heteroaromatic ketones also undergo the 1:1 coupling reaction with a silylacetylene.



(3)



(4)

The findings described above represent the first examples of direct, catalytic addition of otherwise inactive C-H bonds in aromatics across carbon-carbon triple bonds. Much works will be needed to answer the interesting mechanistic questions[14] that have been raised. Right now, however, we are concerning our efforts on expanding the scope of the new catalytic reactions.

Supplementary Material (4 pages) including spectral data of new compounds are available on request to the author by telefax (+81-6-879-7396).

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