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# Fe(OTf)$_3$-Catalyzed Addition of sp C−H Bonds to Olefins

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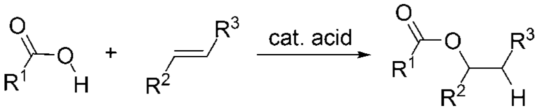
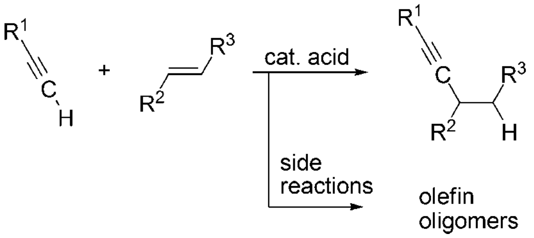
C−C bond formation through cross-coupling between two different organic components is a basic technology in organic synthesis.[1] Examples include the Friedel−Crafts, Mukaiyama aldol, and Diels−Alder reactions and Suzuki−Miyaura coupling. As one of those transformations, the addition of terminal acetylenes to unsaturated bonds is a promising process for introducing an alkynyl group with 100% atom economy. Most reports regarding this category deal with cross-dimerization between acetylenes.[2] Although some papers report acetylene addition to C=C double bonds in the presence of transition-metal catalysts such as palladium,[3] copper,[4] rhodium,[5] and ruthenium,[6] the substrates are limited to reactive olefins such as enones,[3a,5a−c,6a−c] acrylates,[4a,b−d,6c] allenes,[3b−d,5d] 1,3-dienes,[6d,e] cyclopropenes,[3e] and norbornadiene.[3f] No examples of acetylene addition to isolated C=C bonds have been reported.

We recently developed a method for esterification of carboxylic acids through addition to olefins catalyzed by Fe(OTf)$_3$ (eq 1):[7]



(1)

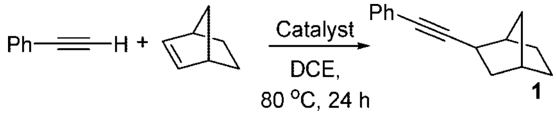
Furthermore, we found a novel acid-catalyzed addition of acetylenes to olefins by using an sp carbon nucleophile instead of an oxygen nucleophile (eq 2): To the best of our knowledge, the only example of acid-catalyzed addition of terminal acetylenes to olefins reported to date used Zn(OTf)$_2$,[8] but the only substrates were Meldrum's acid derivatives. Herein we report a method for acid-catalyzed addition of acetylenes to olefins that does not employ precious-metal catalysts.



(2)

We initially investigated the coupling of norbornene and phenylacetylene in the presence of catalytic triflic acid or its metal salts. Table 1 summarizes the results. The reaction proceeded stereoselectively to exclusively produce the exo isomer **1**, which was determined using NMR spectra.[9] The reverse of the Table 1 reaction did not occur under similar reaction conditions, although **1** was slowly converted to unknown high-boiling compounds. The formation of **1** from such simple starting materials is attractive, as the reaction of an acetylide anion and a *sec*-alkyl halide does not result in the expected alkylation because of the preceding elimination of HX.[10,11] In addition, it is noteworthy that the Pd-catalyzed addition of terminal acetylenes to norbornene (2 equiv) did not proceed, although a similar reaction with norbornadiene resulted in adduct formation at one of the two C=C bonds.[3f]

***Table 1.*** Catalyst Effect on the Addition of Phenylacetylene to Norbornene[a]



| entry | catalyst | yield (%)[b] |
|---|---|---|
| 1 | Fe(OTf)$_3$ | 40 |
| 2 | Fe(OTf)$_3$ | 78[c] |
| 3 | Al(OTf)$_3$ | 36 |
| 4 | Al(OTf)$_3$ | 44[c] |
| 5 | In(OTf)$_3$ | 16 |
| 6 | Sc(OTf)$_3$ | 14 |
| 7 | Cu(OTf)$_2$ | 3 |
| 8 | AgOTf | 0 |
| 9 | AuOTf | 0 |
| 10 | Ph$_3$PAuOTf | 0 |
| 11 | TfOH[d] | 18 |
| 12 | Tf$_2$NH[d] | 0 |

[a] Catalyst (0.08 mmol), norbornene (4 mmol), phenylacetylene (4 mmol), 1,2-dichloroethane (2 mL), 80 °C, 24 h under nitrogen. [b] Determined by GC using decane as the internal standard. [c] Norbornene (4 mmol), phenylacetylene (16 mmol), 168 h. [d] Catalyst (0.24 mmol).

Table 1 shows that the catalytic activities of the triflates greatly depended on the cations. Among the various triflates, the catalytic activities decreased in the order $Fe^{3+} > Al^{3+} \gg H^+, In^{3+}, Sc^{3+} \gg Cu^{2+}, Ag^+$. In general, "hard" acids gave higher yields than "soft" acids such as copper and silver triflates. Among relatively hard acids, Fe(OTf)$_3$ was the best catalyst (entry 1), which is also the case for ester formation from carboxylic acids and olefins.[7] A low material balance in entry 1 is ascribed to olefin oligomerization. When the reaction time and the amount of acetylene were increased, Fe(OTf)$_3$ gave a higher yield of up to 78% (entry 2). On the other hand, employing Al(OTf)$_3$ under reaction conditions similar to those for entry 2 did not improve the product yields (entries 3 and 4). Although Brønsted acids such as TfOH also gave the desired compound in a moderate yield (entry 11), a stronger acid, Tf$_2$NH, failed to produce the adduct (entry 12).

Our procedure, which is depicted in eq 2 and Table 1, is unique and attractive for the following reasons: (i) The reaction proceeds even for isolated C=C double bonds, as in norbornene. (ii) In addition, the reaction is promoted by acid catalysts and does not

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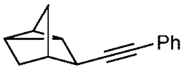
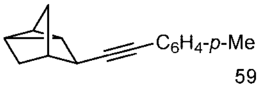
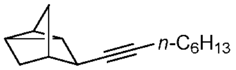
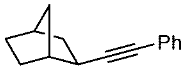
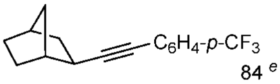
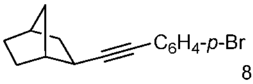
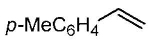
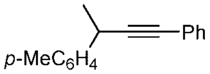
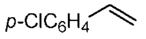
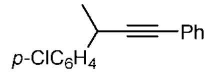
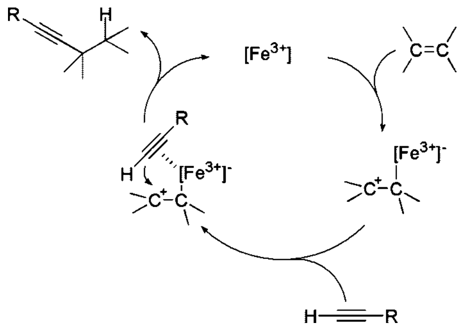
***Table 2.*** Addition of Terminal Acetylenes to Olefins[a]

| entry | olefin | acetylene | product | yield (%) |
|---|---|---|---|---|
| 1 | NBD | Ph—≡—H |  | 93 |
| 2 | NBD | *p*-MeC$_6$H$_4$—≡—H |  | 59 [b] |
| 3 | NBD | *n*-C$_6$H$_{13}$—≡—H |  | 47 [c] |
| 4 | NBE | Ph—≡—H |  | 93<br>85 [d] |
| 5 | NBE | *p*-CF$_3$C$_6$H$_4$—≡—H |  | 84 [e] |
| 6 | NBE | *p*-Br-C$_6$H$_4$—≡—H |  | 89 [e] |
| 7 |  | Ph—≡—H |  | 63 |
| 8 |  | Ph—≡—H |  | 67 [f] |

[a] Olefin (4 mmol), acetylene (16 mmol), Fe(OTf)$_3$ (0.16 mmol), neat, 130 °C, 2 h under nitrogen. Yields were determined by GC using decane as the internal standard. Abbreviations: NBD, norbornadiene; NBE, norbornene. [b] 1.5 h. [c] 24 h. [d] Under air. [e] Chlorobenzene (2 mL), 130 °C, 24 h under nitrogen. [f] 18 h with Fe(NTf$_2$)$_3$ (0.16 mmol).

***Scheme 1.*** Possible Mechanism of Iron-Catalyzed Acetylene Addition to Olefins



include an oxidation−reduction cycle for transition metals. (iii) Moreover, these catalysts are inexpensive, abundant, and less toxic than precious-metal-based catalysts.

Table 2 summarizes the scope of olefins and acetylenes that undergo our procedure. Phenylacetylene added to norbornadiene and norbornene in over 90% yield under the neat conditions at 130 °C (entries 1 and 4). It is noteworthy that the reaction proceeds even under air without a significant decrease in the yield (entry 4, footnote *d*). Tenaglia et al.[3f] recently reported the addition of phenylacetylene to norbornadiene in the presence of phosphapalladacycle. However, similar reactions with norbornene derivatives did not proceed. Although introduction of a methyl group onto phenylacetylene accelerated olefin consumption, it lowered the selectivity and led to olefin-homocoupling byproducts (entry 2). On the other hand, electron-withdrawing acetylenes decelerated the reaction (entry 5). The reaction was also applicable to aliphatic acetylenes in addition to aromatic ones (entry 3). Carbon−halogen bonds are stable under the reaction conditions of Table 2 (entries 5, 6, and 8). The reaction of aliphatic olefins such as 1-octene resulted in complicated products because of facile isomerization of double bonds to internal ones.

A plausible mechanism is shown in Scheme 1: activation of the olefin by coordination of the metal triflate followed by nucleophilic attack of the acetylene or acetylide. The formation of a tricyclic skelton from norbornadiene (Table 2, entries 1−3) is consistent with the mechanism involving cationic intermediates generated through Meerwein−Wagner rearrangement. In addition, the observed following of Markovnikov's rule for styrenes (entries 7 and 8) also fits the cation-based catalytic cycle. On the other hand, a redox mechanism[3−6] is not likely to operate for the iron-catalyzed reaction because oxidative addition to Fe(III) triflate is unusual.

In summary, we have developed a novel acid-catalyzed addition of acetylenes to olefins. The reaction proceeds even under air and does not require precious metals. It should be noted that very recently, the nickel-catalyzed addition of terminal silyl acetylenes to norbornene and CF$_3$- or Et$_2$OC-substituted styrenes has been reported.[12] This reaction requires air-sensitive Ni(COD) and PBu$_3$. The present method will complement the Ni catalysis, depending on the substrates. For example, carbon−bromine bonds, which are sensitive to low-valent transition metals such as Ni(0) and Pd(0), are durable under the Fe(OTf)$_3$ catalysis (entry 6, Table 2).[12]

**Supporting Information Available:** Experimental procedures and spectral data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Although the yields were not satisfactory, compound **1** was obtained by the reaction of an acetylenic sulfone (Ph−C≡C−SO$_2$CF$_3$) and a hydrocarbon (norbornane) at 83 °C. See: Gong, J.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 4486. (b) The related acetylenes were also accessible through the Pd-catalyzed decarboxylation of the corresponding propiolates. See: Rayabarapu, D. K.; Tunge, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13510.
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