

Nickel-catalyzed Reactions between Enone and Two Ethylenes

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In the presence of a catalytic amount of $\text{Ni}(\text{cod})_2$ and PCy_3 , the reaction of (*E*)-1-phenylbut-2-en-1-one (**1a**) with ethylene occurred to give three-component addition products, 1,6-enone **2a** and 1,5-diketone **4a**. The reaction of an enone with two ethylenes gave **2a**. The reaction of two enones with an ethylene gave **4a**. On the other hand, 2-methyl-1-phenylprop-2-en-1-one (**1b**) reacted with two ethylenes selectively to give a mixture of **2b** and **3b**. The reaction might proceed via oxidative cyclization of an enone and an ethylene with nickel(0).

Ethylene is an important industrial feedstock and numerous reactions have been developed to convert ethylene into more valuable chemicals. The hydrovinylation reaction of alkenes catalyzed by transition metal hydride complexes is one of the most useful reactions for the introduction of ethylene into alkenes, however, a limited number of alkenes, such as vinylarenes, cyclic dienes, and norbornenes, are available for hydrovinylation reactions due to the isomerization of terminal alkenes to internal alkenes (eq 1).¹ During the due course of the present study of the formation of hetero-nickelacycles by oxidative cyclization,² we found nickel-catalyzed direct conjugate addition reactions of simple alkenes to enones, which is a very straightforward method to introduce an alkenyl group to the β -carbon of enones by the addition of a carbon–hydrogen bond (eq 2).^{3,4} In this reaction, the oxidative cyclization of alkenes and enones with nickel(0) to give a nickelacycle was proposed as an important key reaction step. On the other hand, in the presence of a nickel catalyst, the reaction of enones with alkynes to give three-component cycloaddition has been reported (eq 3). Ikeda et al. reported nickel-catalyzed reactions of an enone with two alkynes to give cyclohexadiene derivatives.⁵ Montgomery et al. reported nickel-catalyzed intramolecular reactions of an alkyne and two enones to give cyclohexene derivatives.⁶ In a similar reaction with alkenes, Hoberg et al. have reported a nickel-catalyzed three-component addition of a phenyl isocyanate with two ethylenes.⁷ Jamison et al. have reported a nickel-catalyzed reaction of enones with ethylene in the presence of Et_3SiOTf .⁴ However, the three-component

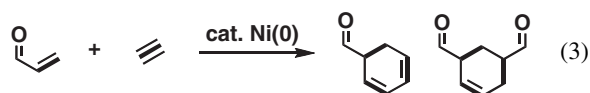
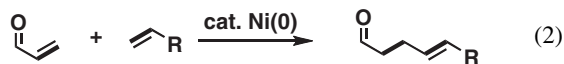
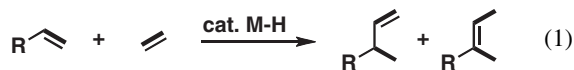
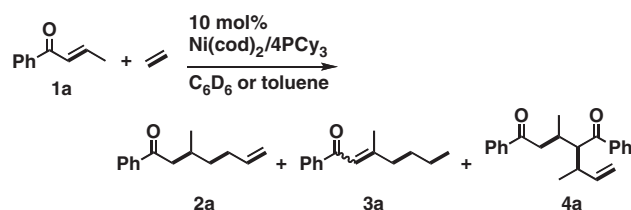


Table 1.

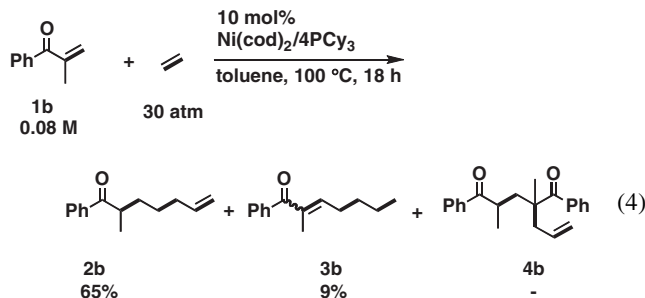


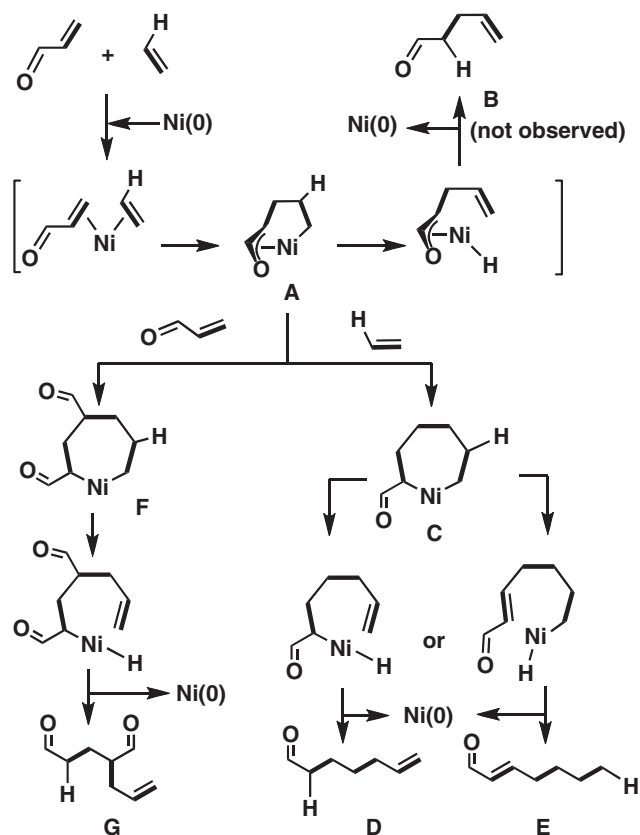
Run	Ethylene	Temp/°C	Time/h	Yield/%		
				2a	3a	4a
1 ^a	5 atm	25	72	7	—	41
2 ^a	5 atm	80	17	20	3	19
3 ^a	8 atm	80	17	30	5	18
4 ^b	30 atm	100	15	43	18	13

^a[**1**] = 0.4 M, C_6D_6 , NMR yield. ^b[**1**] = 0.04 M, toluene, isolated yield.

addition of enones with alkenes to give terminal alkenes has not been reported yet.⁸ Here, we report a nickel-catalyzed three-component addition reaction of enones with ethylene.

In the presence of $\text{Ni}(\text{cod})_2$ and PCy_3 , the reaction of (*E*)-1-phenylbut-2-en-1-one (**1a**) with ethylene (5 atm) at 25 °C in C_6D_6 gave a mixture of 1,6-enone **2a** and 1,5-diketone **4a** (Table 1, Run 1).⁹ Both products were three-component addition compounds. **2a** was the product of an enone and two ethylenes. On the other hand, **4a** was the product of two enones and an ethylene. At higher reaction temperature, the yields of **2a** and its isomer **3a** increased and the yield of **4a** decreased (Run 2). At higher ethylene pressure (8 atm), the yield of **2a** was improved (Run 3). To attain selective formation of **2a** and **3a**, the reaction was carried out under a much higher ethylene pressure (30 atm) at lower concentration of **1a** (0.04 M). A mixture of **2a**, **3a**, and **4a** was obtained in 74% isolated yield, and the selectivity of **2a** and **3a** toward **4a** was also improved (Run 4). Under similar reaction conditions, 2-methyl-1-phenylprop-2-en-1-one (**1b**) also reacted with two ethylenes to give **2b** and **3b** in 65 and 9% isolated yield, respectively (eq 4). In this reaction, the 1,5-diketone product **4b** was not obtained at all, which might be due to the





Scheme 1. A plausible mechanism.

reduced reactivity of the intermediate toward **1b** (see later). Under the same reaction conditions, methyl vinyl ketone, or phenyl vinyl ketone underwent oligomerization. Neither chalcone nor 3-penten-2-one reacted changed.

The reaction might proceed as follows (Scheme 1). The oxidative cyclization of an enone and ethylene with a nickel(0) species generates a η^3 -oxaallylnickelacycle intermediate **A**. The intramolecular oxidative cyclization of an enone and an alkene with nickel(0) to give the corresponding nickelacycle has been reported.³ β -Hydrogen elimination of **A** followed by reductive elimination would give the direct conjugate addition product **B** as reported in the reaction with styrene under the same reaction conditions;³ however, no direct conjugate addition product was obtained in the reaction with ethylene. Only three-component addition products were obtained. Therefore, the reaction of η^3 -oxaallylnickelacycle intermediate **A** with either the second ethylene or the second enone to generate a seven-membered nickelacycle intermediate **C**¹⁰ or **F**¹² might proceed faster than the occurrence of β -hydrogen elimination to give **B**. The intermediate **C** might undergo β -elimination followed by reductive elimination to give a mixture of a 1,6-enone compound **D** and its isomeric 1,2-enone **E**. The conjugate addition of **A** to an enone also generates a seven-membered nickelacycle intermediate **F**¹² followed by β -elimination and reductive elimination to give a 1,5-diketone **G**. As shown in eq 4, **4b** was not obtained in the reaction of **1b** with ethylene, in which nickel enolate intermediate

A might be less reactive due to steric hindrance around the enolate carbon.

In conclusion, the reaction of an enone with two ethylenes to give a 1,6-enone was demonstrated for the first time. This reaction can be regarded as a cross-trimerization of alkenes with ethylene to give a terminal alkene. Moreover, at a lower temperature, the reaction of two enones with an ethylene gave a 1,5-diketone compound as the major product. In both reactions, ethylene reacted with an enone as a vinylation reagent.

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