

Hydrocupration of Alkynes: a Simple Synthesis of (*E,E*)-1,3-Dienes

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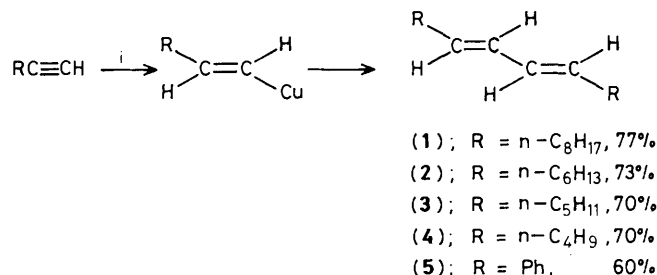
Copper(I) hydride species, prepared *in situ* in tetrahydrofuran using $\text{NaBH}_4\text{-MgBr}_2\text{-Et}_3\text{N-CuCl}$ or $\text{NaH-MgBr}_2\text{-CuCl}$ reagent systems, convert terminal alkynes into (*E,E*)-1,3-dienes in good yields.

The carbocupration of alkynes, developed by Normant, Alexakis, and co-workers, using the RMgX-CuX reagent system is a very useful reaction for the preparation of vinylcopper intermediates for applications in organic synthesis.¹ Surprisingly, the reaction of the copper(I) hydride species with alkynes has not received much attention. The few reports available in the literature indicate that the copper(I) hydride species, prepared using CuX and various metal hydride sources, converts alkynes into alkenes.²⁻⁴ In the course of our studies on non-carbanionic routes for the preparation of transition metal organometallics for applications in organic synthesis,^{5,6} we have observed that the reaction of alk-1-yne with the CuH-MgBr_2 reagent system gives (*E,E*)-1,3-dienes.

In their carbocupration reports, Normant, Alexakis, and co-workers¹ usually write the composition of the reagent system as RCu-MgBr_2 . However, Ashby and co-workers have found that it actually exists in tetrahydrofuran (THF) as aggregates whose composition is dependent on the time and temperature of the reaction.⁷ They also reported that the

yields of the addition product of the 'RCu' species with phenylacetylene increase with addition of MgBr_2 in some cases.⁷ It occurred to us that it may be possible to make the 'CuH' species, produced *in situ* during the decomposition of CuBH_4 in the presence of triethylamine,^{5,8} react with alkynes in the presence of MgBr_2 . In order to examine this possibility we carried out the following experiment: MgBr_2 (20 mmol) was prepared in THF (50 ml) using Mg (40 mmol, excess) and 1,2-dibromoethane (20 mmol). This solution was then added to NaBH_4 (10 mmol) in THF (50 ml) under nitrogen, and the mixture was stirred for 2 h at room temperature and cooled to -20°C . CuCl (15 mmol) and Et_3N (12 mmol) were added followed by dec-1-yne (5 mmol). The contents were stirred at -20°C for 2 h and at room temperature for 40 h. After work-up and chromatography on a silica gel column using hexane as eluant, (*E,E*)-icosa-9,11-diene was isolated in 60% yield. Clearly, the dec-1-yne undergoes hydrocupration with the CuH-MgX_2 ($\text{X} = \text{Br}$ or Cl) reagent.

If the function of the triethylamine in this experiment is just to strip off the 'BH₃' moiety as the corresponding amine-



Scheme 1. Reagents and conditions: i, NaH-MgBr₂-CuCl, THF, -20°C to room temp.

borane complex, it should be possible to utilise NaH as the hydride source. When the procedure was carried out by replacing NaBH₄ with NaH (30 mmol) and using 10 mmol of dec-1-yne in the absence of triethylamine, (*E,E*)-icosa-9,11-diene was isolated in 77% yield.† We have also converted several other alk-1-yne into the corresponding (*E,E*)-1,3-dienes following this procedure (Scheme 1).‡ Presumably, the NaH reacts with MgBr₂ to give magnesium hydride species^{10,11} which in turn react with CuCl to give the reactive CuH-MgX₂ (X = Cl or Br) aggregates. The hydrocupration of the alk-1-yne by this reagent would result in the formation of (*E*)-alk-1-enylcopper species (Scheme 1). Thermal decomposition of these vinylcopper intermediates gives the corresponding (*E,E*)-1,3-dienes. Whitesides and co-workers ob-

† Control experiments indicate that both MgBr₂ and CuCl are necessary for this transformation. All yields reported in this paper are based on the organic substrates utilised.

‡ ¹³C N.m.r. data (CDCl₃) for the (*E,E*)-1,3-dienes: (1) δ 132.3, 130.5, 32.7, 32.0, 29.8, 29.6, 29.5, 22.8, 14.2; (2) δ 132.2, 130.6, 32.8, 32.0, 29.1, 28.2, 27.2, 14.2; (3) δ 132.4, 130.5, 32.8, 32.6, 32.1, 29.4, 22.8, 14.3; (4) δ 132.0, 130.7, 32.2, 31.9, 30.0, 29.7, 22.5, 14.0; (5) δ 137.3, 132.9, 129.4, 128.8, 127.7, 126.5 (m.p. 150°C, lit.⁹ m.p. 152.5°C). The ¹³C n.m.r. spectra of these (*E,E*)-1,3-dienes do not show signals corresponding to the (*E,Z*) or (*Z,Z*)-1,3-dienes or other isomers (if any). Accordingly, these isomers cannot be present in significant amounts in the (*E,E*)-1,3-dienes obtained following the present method. This indicates that hydrocupration using the present reagent system is highly regio- and stereo-specific (Scheme 1).

served the thermal decomposition of (*E*)-prop-1-enylcopper in diethyl ether at 25°C to give the corresponding (*E,E*)-1,3-diene with retention of stereochemistry about the double bond.¹² They showed that free vinyl radicals are not intermediates in this reaction and suggested several other mechanistic pathways which are compatible with their results.¹²

In addition to providing a reagent system for the hydrocupration of alk-1-yne, this method should also serve as a relatively simple alternative procedure to the available methods for the conversion of alk-1-yne into the corresponding (*E,E*)-1,3-dienes.^{9,12-14}

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