Bis(acetylacetonato)copper Catalyzed Cross-coupling Reaction of Alkenyldicyclohexylborane with 1-Bromo-1-alkyne or 3-Bromo-1-propene

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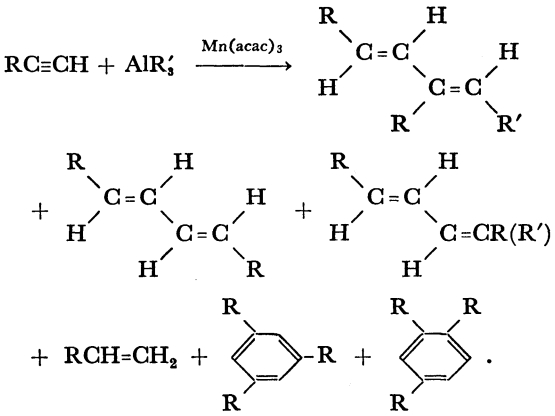
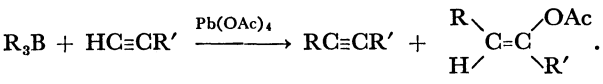
Synopsis. Bis(acetylacetonato)copper is capable of catalyzing cross-coupling reaction of alkenyldicyclohexylborane with 1-bromo-1-alkyne or 3-bromo-1-propene to give conjugated (*E*)-enyne or (*E*)-1,4-diene in a highly stereoselective manner, respectively.

Caporusso *et al.*[1] reported that trialkylaluminium reacted with 1-alkyne in the presence of tris(acetylacetonato)manganese to give a mixture of some unsaturated compounds:

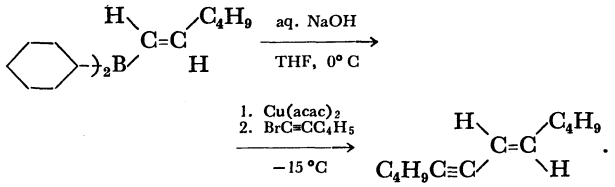


The present authors, on the other hand, have reported of coupling reactions of the alkyl groups of trialkylborane with such groups as SCN,[2,3] SeCN,[3,4] and $OCOCH_3$[5] bonded to some metals. They[6] also reported that trialkylborane reacted with 1-alkyne in the presence of lead(IV) acetate to give an internal alkyne together with an internal enol acetate:



In the course of our investigation on reactions of organoborane with metal complexes, we have come to get interested in the behavior of organoborane in the presence of metal acetylacetonate.

The reaction of trihexylborane with 1-hexyne was first examined in the presence of several metal acetylacetonates. However, such compounds as had been detected in the reaction of trialkylaluminium could not be found at temperatures ranging from −20 to 40 °C; thus 1-bromo-1-hexyne was used instead of 1-hexyne. In this case a considerably clean cross-coupling reaction occurred between trihexylborane and 1-bromo-1-hexyne in the presence of bis(acetylacetonato)copper to give 5-dodecyne in a yield above 60% as based on trihexylborane used.[7] A higher yield of cross-coupling product was obtained when 1-hexenyldicyclohexylborane was treated with aqueous sodium hydroxide and 1-bromo-1-hexyne in the presence of a catalytic amount of bis(acetylacetonato)copper (5%). Thus, 5-dodecene-7-yne, a coupling product of the hexenyl and the hexynyl group, was provided in 75% yield with a high isomeric purity (above 99%):

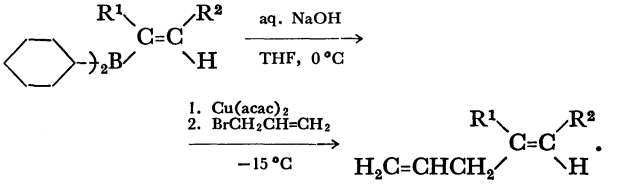


E-configuration of this enyne was assigned from the coupling constant between olefinic protons (J=16 Hz) in ^{1}H NMR spectrum and the absorption band at 965 cm^{-1} in IR spectrum. To obtain a highly pure (*E*)-5-dodecene-7-yne, it is necessary to keep the temperature below −15 °C during the addition of 1-bromo-1-hexyne. Otherwise, some by-products will appear and prevent easy isolation of the enyne from the reaction mixture.[8]

As shown in Table 1, a similar reaction also proceeded without any difficulty which produced the corresponding (*E*)-enyne when an internal alkenyldicyclohexylborane was used as the starting material. Similar results were also obtained when 1-bromo-2-phenylethyne was employed instead of 1-bromo-1-hexyne. High isomeric purities of (*E*)-enyne (above 99%) were obtained in all cases examined. These results suggest that the present reaction may provide a general method for the synthesis of conjugated (*E*)-enyne.

Miyaura *et al.*[9] reported of excellent cross-coupling reactions of alkenyldialkylborane with 1-bromo-1-alkyne; they obtained high yields (72—100%) of conjugated (*E*)-enyne in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium. The present reaction, though inferior to theirs in yield, is comparable in stereoselectivity of reaction.

The present reaction is also applicable to cross-coupling reaction of alkenyldicyclohexylborane with 3-bromo-1-propene; (*E*)-1,4-diene was afforded in a highly stereoselective manner:



Since the cross-coupling reaction of alkenyldialkylborane with 3-bromo-1-propene has already been studied extensively by several workers,[10] any investigation of this coupling reaction was not made with a variety of substrates.

The present bis(acetylacetonato)copper-catalyzed cross-coupling reaction is a new application of this reagent as a catalyst in the reaction of organoborane and seems to be an easy and inexpensive method for the synthesis of conjugated (*E*)-enyne or (*E*)-1,4-diene.

Table 1. $Cu(acac)_2$-catalyzed cross-coupling reaction of alkenyldicyclohexylborane with 1-bromo-1-alkyne or 3-bromo-1-propene

R^1	R^2	R^3	Compound No.	Product and yield/%[a] $R^3C{\equiv}CR^3$ A	B	$H_2C{=}CHCH_2R^3$ A	B
H	Butyl	Butyl	1	75	67		
Ethyl	Ethyl	Butyl	2	83	77		
H	Phenyl	Butyl	3	85	80		
H	Butyl	Phenyl	4	66	55		
Ethyl	Ethyl	Phenyl	5	63	55		
H	Phenyl	Phenyl	6	65	57		
H	Octyl	$BrCH_2CH=CH_2$	7			78	63
H	Phenyl	$BrCH_2CH=CH_2$	8			95	86

a) Based on alkenyldicyclohexylborane employed: A, yield determined by GLC; B, yield determined via isolation by column chromatography.

Experimental

Instruments. IR spectra (film) were recorded with a Hitachi-285 spectrometer. ^1H NMR (60 MHz) spectra (CCl_4) were recorded on a Hitachi R-20A spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer.

Reagents. Cyclohexene and THF were dried over lithium aluminium hydride and distilled before use. 1-Bromo-1-hexyne and 1-bromo-2-phenylethyne were prepared as described in the literature.[11] 1-Hexyne, 1-octyne, phenylacetylene, and 3-bromo-1-propene were dried over molecular sieves 5A. THF solution of BH_3 was prepared by the method described in the literature.[12]

General procedure. A 50 ml round bottomed flask, equipped with a gas inlet for argon, a sample inlet with serum cap, and a magnetic stirring bar, was flushed with argon, and used to prepare dicyclohexylborane by adding 40 mmol of cyclohexene to 20 mmol BH_3 in THF. To the solution, 20 mmol of alkyne was slowly added at 0 °C and the solution was stirred for 3 h at the same temperature. Then, 20 mmol of aqueous sodium hydroxide (2 mol dm^{-3}) was added at 0 °C and stirring was continued for 0.5 h at room temperature. The solution was cooled again to −15 °C, 1 mmol of $Cu(acac)_2$ was introduced into the reaction mixture under a slow argon flow, and then 20 mmol of 1-bromo-1-alkyne or 3-bromo-1-propene was added at the same temperature. After 1 h reaction at −15 °C, the reaction mixture was warmed to room temperature and kept stirred for 20 h, and then the residual organoborane was oxidized with alkaline hydrogen peroxide. The reaction mixture was extracted twice with 30 ml of hexane. The combined extracts were washed twice with NaCl-saturated water and dried over anhydrous calcium chloride. After removal of the solvents under reduced pressure, the reaction mixture was passed through a column packed with silica-gel (Wako-gel Q-50). The products were isolated by elution with hexane.

Analytical data for the products are as follows:

(E)-*5-Dodecen-7-yne* (**1**): n_D^{20} 1.4732; ^1H NMR (CCl_4) δ= 0.88 (6H, t, J=7 Hz), 1.11 (8H, m), 1.83—2.40 (4H, m), 5.27 (1H, d, J=16 Hz), and 5.62—6.13 (1H, m); IR (film) 2230 and 965 cm^{-1}; MS *m/e* 164 (M^+). Found: C, 87.70; H, 12.15%. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%.

(E)-*4-Ethyl-3-decen-5-yne* (**2**): n_D^{20} 1.4677; ^1H NMR (CCl_4) δ=0.70—1.30 (9H, m), 1.30—1.65 (4H, m), 1.65—2.40 (6H, m), and 5.55 (1H, t, J=7 Hz); IR (film) 2210 cm^{-1}; MS *m/e* 164 (M^+). Found: C, 87.68; H, 12.20%. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%.

(E)-*1-Phenyl-1-octen-3-yne* (**3**): n_D^{20} 1.5873; ^1H NMR (CCl_4) δ=0.88 (3H, t, J=7 Hz), 1.10—1.70 (4H, m), 2.13—2.45 (2H, m), 5.99 (1H, dt, J_t=16 Hz and J_d=2 Hz), 6.70 (1H, d, J=16 Hz), and 7.12 (5H, m); IR (film) 2190 and 960 cm^{-1}; MS *m/e* 184 (M^+). Found: C, 91.20; H, 8.72%. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75%.

(E)-*1-Phenyl-3-octen-1-yne* (**4**): n_D^{20} 1.5674; ^1H NMR (CCl_4) δ=0.88 (3H, t, J=Hz), 1.10—1.60 (4H, m), 1.87—2.31 (2H, m), 5.50 (1H, d, J=16 Hz), 5.87—6.40 (1H, m), and 7.05—7.50 (5H, m), IR (film) 2190 and 955 cm^{-1}; MS *m/e* 184 (M^+). Found: C, 91.24; H, 8.69%. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75%.

(E)-*3-Ethyl-1-phenyl-3-hexen-1-yne* (**5**): n_D^{20} 1.5620; ^1H NMR (CCl_4) δ=0.70—1.60 (6H, m), 1.90—2.20 (4H, m), 5.79 (1H, t, J=7 Hz), and 7.05—7.55 (5H, m), IR (film) 2190 cm^{-1}; MS *m/e* 184 (M^+). Found: C, 91.27; H, 8.78%. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75%.

(E)-*1,4-Diphenyl-1-buten-3-yne* (**6**): mp 87 °C; ^1H NMR (CCl_4) δ=6.20 (1H, d, J=16 Hz), 6.92 (1H, d, J=16 Hz), and 7.10—7.50 (10H, m); MS *m/e* 204 (M^+). Found: C, 94.01; H, 5.94%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%.

(E)-*1,4-Undecadiene* (**7**): n_D^{20} 1.4385; ^1H NMR (CCl_4) δ= 0.84 (3H, t, J=7 Hz), 1.10—1.70 (8H, m), 1.80—2.18 (2H, m), 2.50—2.80 (2H, m), and 4.70—6.10 (5H, m),; IR (film) 970 cm^{-1}; MS *m/e* 152 (M^+). Found: C, 86.73; H, 13.23%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%.

(E)-*1-Phenyl-1,4-pentadiene* (**8**): n_D^{20} 1.5513; ^1H NMR (CCl_4) δ=2.83 (2H, t, J=7 Hz), 4.98 (2H, m), 5.45—6.30 (3H, m), and 7.10 (5H, m); IR (film) 965 cm^{-1}; MS *m/e* 144 (M^+). Found: C, 91.55; H, 8.34%. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.93%.

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7) The result of metalacetylacetonate-catalyzed cross-coupling reaction of trialkylborane with 1-alkyne will be reported elsewhere.

8) 1-Cyclohexyl-1-hexyne is a major by-product, which cannot be removed from (*E*)-5-dodecen-7-yne by any simple procedures such as column chromatography and distillation.

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