of triethylamine. The solution was placed in the cell described above and electrolyzed at 0 °C and 105–170 V with the current maintained at 0.25 A for 9 h. The reaction mixture was poured into 350 ml of saturated NaCl solution and extracted with 4 × 100 ml of ether. The solvent was removed and the resultant oil distilled at 120–130 °C (0.15 mm) to produce a solid distillate. Chromatography on neutral alumina with a 1:1 mixture of ether to petroleum ether gave 210 mg of a white, crystalline solid: mp 121–121.5 °C; infrared 1655 cm^{-1}; mass spectrum parent ion *m/e* 246; ultraviolet λ_{max} 241 nm (ϵ 2.14 × 10^4). These data are consistent with the structure of compound **2**. The yield was 11.4%.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.92; H, 9.04.

Reductive Coupling of 2. To 50 ml of acetonitrile were added 200 mg (0.81 mmol) of **2**, a solution of 5 g of tetraethylammonium chloride in 50 ml of acetonitrile, and 13 ml of distilled water. The solution was placed in the electrolysis cell and degassed by bubbling nitrogen through the stirred solution for 45 min. The half-wave reduction potential was determined by polarography to be at −1.7 V (vs. SCE). The preparative reaction was run at −1.80 V (vs. SCE) for 7 h. The acetonitrile was distilled and the residue taken up in 200 ml of 5% NaCl solution and extracted with 3 × 50 ml of ether. The ether was dried and removed under vacuum and the oily residue was placed on a neutral alumina column and eluted with 15% ether in petroleum ether. This yielded 130 mg of a slightly yellowish, crystalline solid: mp 180–181 °C; infrared 1707 cm^{-1}; ^1H NMR 0.93 ppm, s, in $CHCl_3$; 0.97 ppm, s, in C_5H_5N. The NMR spectrum in $CHCl_3$ at −40 °C was essentially unchanged. The ^{13}C NMR in $CDCl_3$ exhibited eight resonances at 213.0, 52.3, 44.7, 41.0, 31.2, 22.1, 19.6, and 15.5 ppm. Mass spectrum: parent ion *m/e* 248. These data identified the product as **3a**. The yield was 81% taking into account recovered starting material (see below).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.95; H, 9.03.

Elution of the alumina with 50% ether–petroleum ether afforded 40 mg of the starting diketone **2**.

Registry No.—**2**, 60410-71-1; **3a**, 60410-72-2; **6**, 487-51-4; **7**, 20653-49-0; **7** diacid, 60410-73-3; **8**, 60410-74-4; **9**, 60410-75-5; **10**, 60410-76-6; ethyl chloroacetate, 105-39-5.

References and Notes

(1) Abstracted from the Ph.D. Dissertation of Richard F. Daley, Emory University, 1976.

(2) J. P. Zimmer, J. A. Richards, J. C. Turner, and D. H. Evans, *Anal. Chem.*, **43**, 1000 (1971), and references cited therein; N. L. Weinberg "Technique of Electro-organic Synthesis", in two parts, "Techniques of Chemistry", Vol. V, A. Weissberger, Ed., Wiley, New York, N.Y., 1975.

(3) W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 1498 (1953).

(4) S. Swann, Jr., and W. E. Garrison, Jr., "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 463.

(5) M. Finkelstein and R. C. Peterson, *J. Org. Chem.*, **25**, 136 (1960).

(6) For example Δ^4-3 keto steroids seem to couple to afford pinacols similar to **5** [P. Kabasakalian and J. McGlotten, *J. Am. Chem. Soc.*, **78**, 5032 (1956)] and even cyclohexenone gives a mixture of β–β coupling and "head to tail" coupling (similar to 4) [E. Touboul, F. Weisbuck, and J. Wiemann, *C. R. Acad. Sci.*, **268**, 1170 (1969).

(7) J. H. P. Utley in the text cited in ref 2, p 793.

Cis Reduction of Acetylenes by Organocopper Reagents[1a]

Jack K. Crandall* and Francois Collonges[1b]

Contribution No. 2864 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

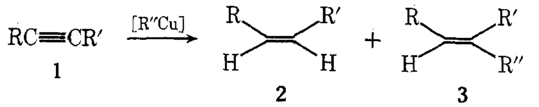
Received May 25, 1976

The stereoselective reduction of several disubstituted acetylenes to the corresponding cis olefins has been effected by an organocopper reagent prepared from CuI and 2 equiv of a primary Grignard reagent. A mechanistic pathway is proposed which involves the generation of a copper hydride species and subsequent cis addition of this intermediate to the acetylene function. Evidence for a vinylcopper intermediate of type **13** was obtained by trapping experiments with D_2O and allyl bromide. Phenyl-substituted acetylenes also undergo competitive addition of the alkylcopper reagent when THF is employed as the solvent (but not in ether solution). On the other hand, 3-phenyl-2-propyn-1-ol (**11**) shows only a regioselective trans addition of alkylcopper reagents leading to allylic alcohols of type **10**.

Organocopper reagents are known to add to terminal[2] and certain functionalized acetylenes[3] in synthetically useful reactions usually with high regio- and stereoselectivity. In connection with a study of related intramolecular analogues,[4] we have found that organocopper reagents also react with simple disubstituted acetylenes under some conditions. The predominant reaction in this case is reduction of the acetylene to the corresponding cis olefin, a highly stereoselective transformation of some synthetic potential. In several instances, addition of the organometallic species also takes place in the same fashion as with terminal acetylenes.[2]

Results

The organocopper reagent obtained by mixing *n*-BuMgBr and CuI in a 2:1 ratio at −35 °C in THF solution undergoes obvious decomposition upon warming to room temperature. The inclusion of 1-phenylpropyne (**1a**) in a fivefold excess of this reagent during the warming process resulted in 98% conversion of **1a** to a 68:30 mixture of (*Z*)-phenylpropene (**2a**) and (*E*)-2-methyl-1-phenyl-1-hexene (**3a**) after hydrolysis at the end of a 1-h reaction period. Under these conditions the cis reduction product **2a** was formed with a minimum of 99% stereoselectivity, although allowing the reaction mixture to stand for 24 h before hydrolysis resulted in contamination of the **2a** with 6% of **4a**, its *E* isomer. Quenching a similar reaction with D_2O gave **2a** with the incorporation of 41% deuterium, exclusively at C-1 as determined by NMR analysis. The addition product **3a** incorporated 86% deuterium in this experiment.



The structure of **3a** was established by comparison with an authentic sample obtained from the Wittig reaction[5] of the ylide derived from benzyltriphenylphosphonium chloride with 2-hexanone. The isomeric olefins produced in this fashion were separated by GLC and examined by ^{13}C NMR in order to secure stereochemical assignments. Thus, *E* isomer **3a** displays its allylic methyl at higher field (17.5 ppm) than that of the *Z* isomer **5** (23.8 ppm), whereas the allylic methylene carbon appears at higher field for **5** (32.0 ppm) than it does for **3a** (40.2 ppm). These assignments are based on the expecta-

Table I. Reactions of Acetylenes with Organocopper Reagents

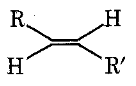
Acetylene						Products, %	
1	R	R′	R″MgX	Time, h	Conversion, %	2	3
a	Ph	CH_3	*n*-Bu[a]	1	98	68	30
			n-Bu	0.75	100	100	
			i-Pr	48	35	35	
			t-Bu	15	0		
			Et	1	99	99	
b	Ph	Ph	*n*-Bu[a]	5	100	30	70
			Et	4	65	65	
c	*n*-C_5H_{11}	CH_3	*n*-Bu	6	80	80	
d	*t*-Bu	*t*-Bu	*n*-Bu		0		

[a] THF solvent.

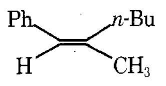
tion that the group cis to the phenyl substituent will have its carbon shifted to higher field owing to steric interactions.[6]

The addition reaction leading to **3a** has not heretofore been observed for disubstituted acetylenes of a nonfunctionalized type except for the intramolecular examples recently reported by us.[4] Interestingly, this product predominates during the initial phases of the reaction as observed by GLC monitoring of the course of the reaction. However, attempts to find experimental conditions under which the addition process predominates at high conversions of acetylene have thus far proven unsuccessful, since decomposition of the reagent (and the resulting reduction of **1a** to **2a**) occurs at the minimum temperatures needed for the formation of **3a**.

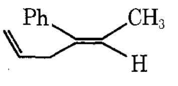
In an effort to develop a more efficient reducing system, several other Grignard reagents were utilized; in these experiments diethyl ether was used as the solvent. The organocopper reagent derived from *t*-BuMgBr decomposed more readily as anticipated, but no reduction of **1a** was observed. The reagent prepared from *i*-PrMgBr gave reduction of **1a** to **2a** without competing addition, but conversions were low. However, utilization of EtMgBr in the general procedure resulted in essentially complete conversion to **2a**. These experiments and related ones described below suggested that THF might be promoting the addition reaction, and, indeed, an experiment using *n*-BuMgBr *in diethyl ether* also gave clean reduction of **1a** to **2a** without the formation of appreciable amounts of **3a**. The reaction product from a similar experiment was treated with allyl bromide in the presence of HMPA prior to hydrolysis, whereupon 40% of the alkylated product **6** was obtained in addition to **2a** (57%). Compound



4



5

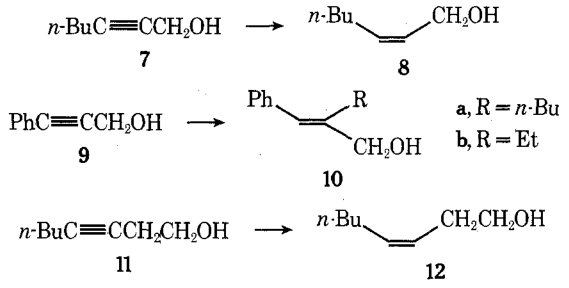


6

6 is assigned the *Z* configuration on the basis of the proton chemical shift of the allylic methyl which is found at high field (1.56 ppm) relative to the corresponding methyl (1.70 ppm) in the known *E* isomer.[7] The shielding effect of the *cis*-phenyl substituent in **6** accounts for this upfield shift.[8] An attempt to alkylate the intermediate organometallic species with CH_3I was not successful. Interestingly, the lithium cuprate derived from *n*-BuLi did not react with **1a** in THF–pentane even on prolonged treatment.

Other acetylenes behave in an analogous fashion. Thus, diphenylacetylene (**1b**) was converted stereoselectively to *cis*-stilbene (**2b**) by the *n*-BuMgBr-derived reagent in THF, although the addition compound **3b**[9] was the major product under these conditions. Only reduction to **2b** was observed in an experiment using EtMgBr in ether, albeit with a lower conversion of **1b**. 2-Octyne (**1c**) gave an 80% conversion exclusively to (*Z*)-2-octene (**2c**) with *n*-BuMgBr in ether. Highly hindered di-*tert*-butylacetylene (**1d**) was not reactive under similar conditions.

Propargyl alcohols also react with organocopper reagents. Thus, the reagent prepared from EtMgBr promoted an efficient conversion of 2-heptyn-1-ol (**7**) to (*Z*)-2-hepten-1-ol (**8**) (58%) and a mixture of several volatile hydrocarbons (which was not further characterized except to note an allene band at 1960 cm^{-1} in the ir). On the other hand, 3-phenyl-2-propyn-1-ol (**9**) gave the trans addition product **10a** in high yield



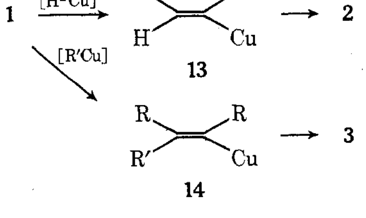
upon treatment with the *n*-butyl reagent in THF solution. The same product has recently been reported from the reaction of *n*-BuLi to **9**.[10] The identity of the two products was demonstrated by direct comparison. A similar addition leading to **10b** was obtained upon reacting **9** with the EtMgBr-derived reagent in ether solution. The stereochemical assignment for **10b** follows from the great similarity in the relevant NMR signals of both the proton and ^{13}C spectra of **10a** and **10b**. The high regioselectivity in these clean addition reactions is noteworthy, as is the trans nature of the addition process.

Finally, homopropargyl alcohol **11** was partially converted to the cis olefinic alcohol **12** by an excess of the *n*-butyl reagent in ether. The stereochemistry was assigned on the basis of the magnitude of the coupling constant ($J = 10$ Hz) between the olefinic protons in the NMR spectrum of **12**.[11]

Discussion

The reductions of the type **1** → **2** appear to offer some promise for the highly stereoselective reduction of simple disubstituted acetylenes to cis olefins. The reaction seems to be generally applicable, although the large excess of reagent required for high conversions may be undesirable in some synthetic applications. The competing addition reaction (**1** → **3**) can generally be suppressed by choosing appropriate experimental conditions, notably the use of ether as a solvent.

The reduction process probably involves the in situ generation of a copper hydride species of undefined structure which adds to the acetylene function in a cis manner. The resulting vinylcopper intermediate **13** is then transformed into the



observed product **2**. The decomposition of alkylcopper species to olefin and copper hydride is a well-precedented process[12] and attention has recently been focused on the importance of copper hydride reactions in side processes attending organocuprate conversions.[13] The cis mode of the copper hydride addition is analogous to the usual stereochemistry for alkylcopper additions to acetylenes.[2,3] A number of copper hydride reagents have been reported during the course of this study,[14,15] and in a couple of instances, these reagents were shown to reduce acetylene functions.[15] Such reductions are predominantly cis, but the reported stereoselectivities are significantly lower than those observed in the present work, where trans isomers were not usually detected. Concrete evidence for an intermediate vinylcopper species is provided by the trapping experiments on **1a** with D_2O and allyl bromide. These experiments also reveal a regioselectivity for **1a** which adds copper hydride in such a manner as to preferentially place the copper at the phenyl-substituted carbon. However, the inefficiencies of the trapping experiments with **1a** indicate that substantial conversion of **13** to olefinic product occurs prior to hydrolysis. This is attributed to the reaction of **13** with additional copper hydride resulting in substitution of the vinylic copper by hydrogen. Such substitutions are documented for a range of organocopper compounds, and have been shown to proceed with retention of configuration at an olefinic center.[16] Unfortunately this process limits the potential of intermediate **13** insofar as further synthetic transformations are concerned.

The addition reaction leading to products of type **3** is favored by conjugating phenyl substituents and by the use of THF as a solvent. The D_2O quenching experiment with **1a** supports the notion that this product is formed by the regio- and stereoselective addition of the organocopper reagent to yield an intermediate of type **14**. This more hindered vinylcopper derivative is less susceptible than **13** to further reaction with copper hydride as indicated by the higher incorporation of deuterium in **3a** relative to **2a**.

The results with the acetylenic alcohols present an interesting contrast. The alkyl-substituted compounds **7** and **11** undergo reduction in a clean cis fashion much like the unfunctionalized alkynes, although the propargyl compound is more reactive and suffers competing side reactions. On the other hand, the phenyl-substituted propargyl alcohol **9** not only shows a high propensity for regioselective addition of the alkylcopper reagent, but involvement of the hydroxyl function results in overall trans addition. While this stereochemistry contrasts with that of the addition reactions of simple alkynes, it is nonetheless characteristic of the additions of *n*-butyllithium[10] and certain Grignard reagents[17] to propargyl alcohols. Finally, a recent publication reports similar additions of a range of Grignard reagents to variously substituted propargyl alcohols in the presence of catalytic amounts of CuI.[18] Moreover, these catalyzed additions result in organomagnesium intermediates which can be trapped in high yield, a feature of obvious advantage in synthetic work.

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were recorded on CCl_4 solutions relative to internal Me_4Si using Varian EM-360 and HR-220 spectrometers for proton measurements and a Varian XL-100 for ^{13}C determinations. Infrared (ir) spectra were obtained on liquid films with Perkin-Elmer Model 137 Infracord and Unicam SP 1000 instruments. Mass spectra were recorded at 70 eV on a Varian-MAT CH-7 spectrometer. Gas chromatography (GLC) was performed on Aerograph 600C, 600D, 1200, and A700 instruments using an analytical column of 20% Carbowax 20M on Chromosorb W and a preparative column of 20% PDEAS on Chromosorb W.

Reaction of 1-Phenylpropyne (1a) with Organocopper Reagents. A. To a suspension of 2.3 g (12 mmol) of anhydrous CuI in 12 ml of dry THF under a N_2 atmosphere at −35 °C was added dropwise 27.5 ml (24 mmol) of a 0.87 M solution of *n*-BuMgBr in THF. To the light yellow suspension thus obtained was added 464 mg (4 mmol) of **1a** and the reaction mixture was allowed to warm to room temperature. Above 15 °C the suspension turned brown and then black. The course of the reaction was monitored by removing aliquots periodically, hydrolyzing with aqueous NH_4Cl, washing with water, and analyzing by GLC. After 15 min of warming (temperature >15 °C) a 54:21:26 mixture of **1a**:**2a**:**3a** was observed; after 30 min the mixture was 9:64:27 and after 45 min it was 2:68:30. However, no reaction had occurred at 0 °C, prior to visible decomposition of the reagent. Less than 1% of **4a** was present in the above mixtures as demonstrated by GLC comparison with an authentic sample. Upon standing for 24 h the amount of **3a** had decreased substantially relative to the 1-phenylpropene which contained 6% of **4a** at this point. The reaction was worked up as described for the aliquots and the products were isolated by GLC and characterized spectroscopically. Compound **4a** was identified on the basis of its GLC retention time only. (*E*)-2-Methyl-1-phenyl-1-hexene (**3a**) showed ir 1650 and 908 cm^{-1}; NMR (220 MHz) δ 7.2–6.9 (m, 5), 6.13 (s, 1), 2.11 (t, 2, $J = 7$ Hz), 1.79 (s, 3), 1.5–1.2 (m, 4), and 0.92 (t, 3, $J = 7$ Hz); ^{13}C NMR δ 137.8, 128.3, 127.4, 125.3, 124.9, 40.1, 30.0, 22.2, 17.5, and 13.9; mass spectrum *m/e* (rel intensity) 175 (7), 174 (55), 145 (10), 132 (22), 131 (100), 129 (13), 118 (14), 117 (24), 116 (13), 115 (21), 91 (42), and 77 (5); exact mass 174.140 (calcd for $C_{13}H_{18}$, 174.1409). This material was identical in all respects with the synthetic sample described below. Isomer **5** was not observed by GLC.

B. An identical reaction was hydrolyzed with D_2O after 1 h. The products were isolated by GLC and analyzed for deuterium incorporation by NMR integration. In this fashion 41% deuterium label exclusively at C-1 was found for **2a** and 86% was present in the **3a**.

C. A similar reaction was performed by adding 0.23 g (2 mmol) of **1a** to the reagent prepared from 1.9 g (10 mmol) of CuI in 15 ml of ether and 23.8 ml (20 mmol) of a 0.84 M solution of *n*-BuMgBr in ether at −40 °C. Proceeding as described above resulted in the disappearance of **1a** with concomitant formation of **2a** which was complete after 45 min as determined by GLC. No appreciable amounts of products with longer retention times were observed.

D. A similar reaction was performed on 0.46 g (4 mmol) of **1a** using the reagent prepared from 2.3 g (12 mmol) of CuI and 26 ml (24 mmol) of 0.92 M *n*-BuMgBr in ether. After the starting material had disappeared a solution of 6 g of allyl bromide in 5 ml of hexamethylphosphorous triamide was added. After 4 h at room temperature the reaction was worked up in the usual fashion. GLC analysis of the product showed **2a**, **3a**, and **6** in the proportions 57:3:40. (*Z*)-4-Phenyl-1,4-hexadiene (**6**) showed ir 1648, 995, 960, and 910 cm^{-1}; NMR δ 7.2 (s, 5), 6.2–5.3 (m, 2), 5.2–4.7 (m, 2), 3.05 (d, 2, $J = 6$ Hz), and 1.56 (d, 3, $J = 7$ Hz); mass spectrum *m/e* (rel intensity) 158 (56), 143 (50), 129 (100), 128 (48), 117 (42), 115 (75), 91 (43), and 77 (20); exact mass 158.109 (calcd for $C_{12}H_{14}$, 158.1096).

E. To a suspension of 2.3 g (12 mmol) of CuI in 12 ml of ether at −30 °C was added 28 ml (24 mmol) of 0.86 M EtMgBr in ether. The resulting yellow-green suspension turned black upon warming to room temperature. At a temperature of about 10 °C, 0.46 g (4 mmol) of **1a** was added to this warming mixture. After 1 h essentially complete conversion to **2a** had occurred. Neither **4a** nor longer retention time products were visible by GLC in significant amounts.

F. To the reagent prepared from 3.8 g (20 mmol) of CuI and 50 ml (40 mmol) of a 0.8 M solution of *i*-PrMgBr in ether was added 0.46 g (4 mmol) of **1a**. After reaction for 48 h GLC analysis showed a 65:35 mixture of **1a** and **2a**. No products with longer GLC retention times were detected.

G. To a solution of 53 ml (24 mmol) of 0.45 M *t*-BuMgBr in ether was added in portions 2.3 g (12 mmol) of CuI at −20 °C under a nitrogen atmosphere. After stirring for 10 min 0.46 g (4 mmol) of **1a** was added and the mixture was allowed to warm to room temperature. Analysis by GLC after 15 h showed only unreacted **1a**.

H. To a suspension of 4 g (21 mmol) of CuI in 40 ml of THF at −30 °C was added 30 ml (40 mmol) of a 1.3 M solution of *n*-BuLi in pentane. After 30 min 0.47 g (4 mmol) of **1a** was added, and the reaction mixture was allowed to warm to room temperature and then heated to reflux. Analysis of an aliquot showed only starting material after 17 h.

(*E*)-and (*Z*)-2-Methyl-2-phenyl-1-hexene (3a and 5). A suspension of 56% NaH in mineral oil (3.3 g, 77 mmol) was washed several times with dry pentane to remove the mineral oil, 115 ml of Me_2SO was added, and the mixture was heated to 80 °C for 45 min under a N_2 atmosphere. The resulting solution was cooled and 30 g (77 mmol) of benzyltriphenylphosphonium chloride was added, followed after 10 min by 7.7 g (77 mmol) of 2-hexanone. After 12 h at 60 °C the mixture was cooled and poured into ice–water, pentane was added, and the solid precipitate was removed by filtration and washed with pentane. The filtrate was separated, washed with water, dried ($MgSO_4$), and concentrated. Unreacted 2-hexanone was removed from the resulting product by distillation and the residual oil containing a 6:4 mixture of (*E*)- and (*Z*)-2-methyl-1-phenyl-1-hexene was separated by GLC. The *Z* isomer **5** showed ir 1650 cm^{-1}; NMR (220 MHz) δ 7.2–6.9 (m, 5), 6.13 (s, 1), 2.15 (t, 2, $J = 7$ Hz), 1.82 (s, 3), 1.5–1.2 (m, 4), and 0.87 (t, 3, $J = 7$ Hz); ^{13}C NMR δ 138.2, 137.9, 128.1, 127.4, 125.5, 125.3, 31.9, 30.0, 23.8, 22.5, and 13.8; mass spectrum *m/e* (rel intensity) 175 (7), 174 (59), 145 (11), 132 (21), 131 (100), 129 (13), 118 (14), 117 (29), 116 (13), 115 (20), 91 (37), and 77 (5); exact mass 174.140 (calcd for $C_{13}H_{18}$, 174.1409).

Reaction of Diphenylacetylene (1b). A. To the reagent prepared as described above from 2.85 g (15 mmol) of CuI and 35 ml of 0.87 M *n*-BuMgBr in THF was added 0.53 g (3 mmol) of **1b**. Warming and workup as usual gave after 5 h at room temperature a 30:70 mixture of *cis*-stilbene and (*Z*)-1,2-diphenyl-1-hexene (**3b**):[9] NMR δ 7.3–6.9 (m, 5), 6.4 (s, 1), 2.5 (t, 2, J = 7 Hz), 1.7–1.1 (m, 4), and 0.94 (t, 3, J = 7 Hz). No evidence for *trans*-stilbene or the *E* isomer of **3b** was found by GLC or spectral examination.

B. Performing a similar reaction on 0.53 g (3 mmol) of **1b** with the reagent prepared from 1.72 g (9 mmol) of CuI and 21 ml (18 mmol) of a 0.86 M solution of EtMgBr in ether gave upon the usual workup after 4 h a 35:65 mixture of **1b** and **2b**. No significant products of longer retention times were observed by GLC.

Reaction of 2-Octyne (1c). A reaction of 0.44 g (4 mmol) of **1c** with the reagent prepared from 3.8 g (20 mmol) of CuI and 43.5 ml (40 mmol) of 0.92 M *n*-BuMgBr in ether gave a 20:80 mixture of **1c** and **2c**. No trans isomer **4c** was observable by GLC. (*Z*)-2-Octene (**2d**) showed ir 3030, 1665, and 690 cm^{-1}; NMR δ 5.8–5.1 (m, 2), 2.2–1.8 (m, 2), 1.6 (d, 3, J = 6 Hz), 1.4–1.1 (m, 6), and 0.89 (t, 3, J = 6 Hz).

Reaction of Di-*tert*-butylacetylene (1d). Treating 1 equiv of **1d** with the reagent prepared from 7.5 equiv of CuI and 15 equiv of *n*-BuMgBr in ether in the usual manner for 2 days gave only unchanged starting material.

Reaction of 2-Heptyn-1-ol (7). Reaction of 0.448 g (4 mmol) of **7** with the reagent prepared from 2.3 g (12 mmol) of CuI and 27.5 ml (24 mmol) of 0.86 M EtMgBr in ether in the usual manner for 4 h resulted in a mixture of **8** (58% yield by GLC) and several volatile products which distilled with the ether. These were not further characterized except to note a band at 1960 cm^{-1} in the ir indicating the presence of an allene. (*Z*)-2-Hepten-1-ol (**8**) showed ir 3400, 3030, 1650, and 1010 cm^{-1}; NMR δ 5.8–5.3 (m, 2), 4.1 (d, 2, J = 6 Hz), 2.3–1.9 (m, 2), 1.6–1.1 (m, 4), and 0.9 (t, 3, J = 6 Hz).[19] The *E* isomer was not present to the limit of detection by NMR.

Reaction of 3-Phenyl-2-propyn-1-ol (9). The usual reaction of 0.53 g of **9** with the reagent prepared from 5 equiv of CuI and 10 equiv of *n*-BuMgBr in THF for 5 h resulted in essentially complete conversion to (*E*)-2-(*n*-butyl)-3-phenyl-2-propen-1-ol (**10a**):[10] ir 3400, 3030, 1650, 1030, 910, 745, and 700 cm^{-1}; NMR (C_6D_6, 220 MHz) δ 7.23 (d, 2), 7.13 (t, 2) 7.07 (t, 1), 6.55 (s, 1), 4.03 (s, 2), 2.52 (s, 1), 2.25 (t, 2, J = 7 Hz), 1.36 (quint, 2, J = 7 Hz), 1.16 (sext, 2, J = 7 Hz), and 0.77 (t, 3, J = 7 Hz); ^{13}C NMR δ 142.2, 137.6, 128.4, 127.8, 126.1, 125.2, 66.4, 30.4, 28.3, 22.8, and 13.9; mass spectrum *m/e* (rel intensity) 190 (20), 148 (25), 133 (98), 130 (20), 129 (49), 128 (20), 117 (52), 116 (14), 115 (60), 105 (39), 92 (31), 91 (100), and 77 (22). There was no spectroscopic evidence for the presence of the *Z* isomer.

A similar reaction of 0.53 g of **9** with the reagent prepared from 3 equiv of CuI and 6 equiv of EtMgBr in ether for 4 h gave complete conversion to a product which was 96% (*E*)-2-ethyl-3-phenyl-2-propen-1-ol (**10b**): ir 3400, 3030, 1660, 1020, 910, 745, and 700 cm^{-1}; NMR δ 7.2 (s, 5), 6.46 (s, 1), 4.15 (s, 2), 3.2 (s, 1), 2.25 (q, 2, J = 7 Hz), and 1.10 (t, 3, J = 7 Hz); ^{13}C NMR 143.2, 137.3, 128.3, 127.9, 126.2, 124.5, 66.0, 21.6, and 12.9.[18] There was no spectroscopic evidence for the presence of the *Z* isomer.

Reaction of 3-Octyn-1-ol (11). A reaction of 0.50 g of **11** with the reagent from 5 equiv of CuI and 10 equiv of *n*-BuMgBr in ether was processed after 24 h to give a 65:35 mixture of **11** and (*Z*)-3-octen-1-ol (**12**): ir 3400, 3030, 1655, and 1045 cm^{-1}; NMR (220 MHz) δ 5.43 (d of t, 1, J = 10, 6.5 Hz), 5.26 (d of t, 1, J = 10, 6.5 Hz), 3.49 (t, 2, J = 6.5 Hz), 2.23 (q, 2, J = 6.5 Hz), 2.03 (m, 2), 1.4 (s, 1), 1.32 (m, 4), and 0.89 (t, 3, J = 6 Hz).[20] There was no evidence for the presence of the *E* isomer in the ir or NMR.

Registry No.—**1a,** 673-32-5; **1b,** 501-65-5; **1c,** 15232-76-5; **2d,** 7433-78-5; **3a,** 60428-21-9; **3b,** 5041-40-7; **5,** 60428-22-0; **6,** 60428-23-1; **7,** 20739-58-6; **8,** 55454-22-3; **9,** 1504-58-1; **10a,** 60428-24-2; **10b,** 56407-97-7; **11,** 14916-80-4; **12,** 20125-84-2; benzyltriphenylphosphonium chloride, 1100-88-5; pentane, 109-66-0; R″Cu (R″ = Bu), 34948-25-9; R″Cu (R″ = *i*-Pr), 55883-86-8; R″Cu (R″ = *t*-Bu), 56583-96-1; R″Cu (R″ = Et), 18365-11-2.

References and Notes

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) Recipient of a NATO grant.

(2) J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *J. Organomet. Chem.*, **77**, 269, 281 (1974); J. F. Normant, G. Cahiez, M. Bourgain, C. Chuit, and J. Villieras, *Bull. Soc. Chim. Fr.*, 1656 (1974), and references cited therein; P. L. Coe and N. E. Milner, *J. Organomet. Chem.*, **70**, 147 (1974).

(3) J. F. Normant, *Synthesis*, 63 (1972); G. H. Posner, *Org. React.*, **19**, 1 (1972). See also W. F. Truce and M. J. Lusch, *J. Org. Chem.*, **39**, 3174 (1974); J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **94**, 14 (1975), and references cited therein.

(4) J. K. Crandall, P. Battioni, J. T. Wehlacz, and R. Bindra, *J. Am. Chem. Soc.*, **97**, 7171 (1975).

(5) A. Maercker, *Org. React.*, **14**, 270 (1965).

(6) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 80.

(7) G. Hata and D. Aoki, *J. Org. Chem.*, **32**, 3754 (1967).

(8) H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965).

(9) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963).

(10) L. I. Olsson and A. Claesson, *Tetrahedron Lett.*, 2161 (1974).

(11) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3d ed, Wiley, New York, N.Y., 1974, p 226.

(12) G. M. Whitesides, E. R. Stredronsky, C. P. Casey, and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **92**, 1426 (1970).

(13) H. O. House and J. C. DuBose, *J. Org. Chem.*, **40**, 788 (1975).

(14) R. K. Boeckmann, Jr., and R. Michalak, *J. Am. Chem. Soc.*, **96**, 1623 (1974); E. C. Ashby, T. F. Korenowski, and R. D. Schwartz, *J. Chem. Soc., Chem. Commun.*, 157 (1974); S. Masamune, P. A. Rossy, and G. S. Bates, *J. Am. Chem. Soc.*, **95**, 6452 (1973); S. Masamune, G. S. Bates, and P. E. Georghiou, *ibid.*, **96**, 3686 (1974).

(15) T. Yoshida and E. Negishi, *J. Chem. Soc., Chem. Commun.*, 762 (1974); M. F. Semmelhack and R. D. Stauffer, *J. Org. Chem.*, **40**, 3619 (1975); P. Vermeer, J. Meijer, C. Eylander, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **95**, 25, (1975).

(16) G. M. Whitesides, J. San Filippo, Jr., E. R. Stredronsky, and C. P. Casey, *J. Am. Chem. Soc.*, **91**, 6542 (1969).

(17) F. W. von Reim and H. G. Richey, *Tetrahedron Lett.*, 3777, 3781 (1971).

(18) B. Jousseaume and J. G. Duboudin, *J. Organomet. Chem.*, **91**, C1 (1975).

(19) L. F. Hatch, H. D. Weiss, and T. P. Li, *J. Org. Chem.*, **26**, 61 (1961).

(20) H. R. Sonawane, M. S. Wadig, and B. C. Subba Rao, *Indian J. Chem.*, **6**, 297 (1968).