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Reaction of 1-bromo-1,2-dienes with alkylcuprates as a regio- and stereo-selective route to acetylenic or allenic compounds *

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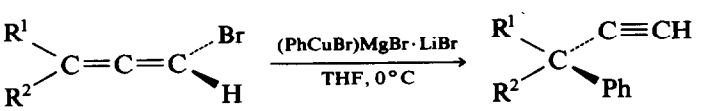
Abstract

Alkylcuprates react with 1-bromo-1,2-dienes to give allenic and/or acetylenic products. The selectivity of the crosscoupling is markedly dependent on the nature of the copper reagent, which plays a prominent role in determining both the regio- and the stereo-chemistry. The preparative aspects of these copper-induced reactions are discussed and their possible mechanism discussed.

Introduction

Allenic compounds have become versatile reagents in preparative organic chemistry and the number of the synthetic applications is rapidly growing [1]. Our recent studies on the regio- and the stereo-chemistry of the reactions between allenic bromides, **1** and organometallic derivatives (of Mg, Zn, Al, Cu) [2] have led to a useful method for the preparation of chiral 3-phenyl-1-alkynes involving use of the complex phenyl-copper agent (PhCuBr)MgBr · LiBr [2d], made in THF at 0 °C from equimolar amounts of PhMgBr and $LiCuBr_2$ [3]. The reaction proceeds via a predominant 1,3-*anti* displacement to give the acetylenic compounds in 70–90% yield with 83–100% stereoselectivity (eq. 1) [2d,4].



(1)

It is noteworthy that the regioselectivity of the phenylation process may be drastically altered by using other types of phenylcopper reagents, such as Ph_2CuLi and Ph(CN)CuLi [2d]. We report here some interesting aspects of the dynamics and the stereochemistry of the coupling reactions between compounds **1** and aliphatic

* Dedicated to the memory of Professor P. Pino.

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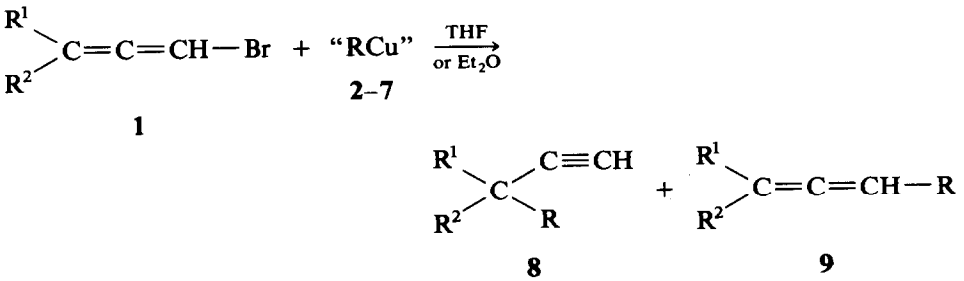
organocopper reagents, which appear somewhat attractive for preparation of acetylenic and allenic compounds and for a mechanistic study of the mode of action of the organometallic species [5]. Little information is available in the literature on this latter aspect; Landor and co-workers [6] concluded that the reactions of 3-substituted and 3,3-disubstituted 1-bromoallenes with lithium dialkylcuprates, R_2CuLi, give 1-alkyl allenes via direct substitution, while Corey [7] observed that cyanocuprates, R(CN)CuLi, react with 1,3-disubstituted-1-bromoallenes to form mainly internal alkynes. In this latter case, a high *anti* stereochemistry was also observed [7].

Results and discussion

When two equivalents of the organocopper reagents **2–7**, prepared by standard methods [6–9], are allowed to react with the bromoallenes **1**, in tetrahydrofuran or diethyl ether solution, a mixture of the two coupling products, the alkyne **8** and the allene **9**, is generally obtained (Scheme 1). The progress of the reactions was monitored by GLC analysis, and the products were identified either by comparison of their GLC retention times with those of authentic samples [2], or by spectroscopic methods.

The results obtained in reactions with the 3,3-dialkyl-1-bromoallenes **1e–g** as model substrates showed clearly that the nature of the copper reagent plays a prominent role in determining both the reaction rate and the regiochemistry of the displacement process (Table 1). In particular, in reactions with the butylcuprates **3–7** the conversion of the substrates was almost complete within 1 h at −40 to −70 °C, whereas the n-butyl copper **2b** under the same conditions reacted only slowly with **1f** and a high conversion (73%) was achieved only after 12 h at a temperature of −10 °C (entry 1). On the other hand, while the reactions of **1e** with



("RCu" = RCu·$MgBr_2$ (**2**); $R_2CuMgBr$ (**3**); 5%CuBr–RMgBr (**4**); R_2CuLi (**5**); R(CN)CuLi (**6**); (RCuBr)MgBr·LiBr (**7**))

1	R^1	R^2	2–7	R
a	H	Me	**a**	Et
b	H	Et	**b**	^{n}Bu
c	H	^{i}Pr	**c**	^{n}C_7H_{15}
d	H	^{t}Bu	**d**	^{i}Bu
e	Me	Et	**e**	^{i}Pr
f	Me	^{n}Pr	**f**	^{t}Bu
g	Me	^{t}Bu		

Scheme 1.

Table 1

Reactions of organocopper reagents **2–7** with 3,3-dialkyl-1-bromo-1,2-dienes $R^2(Me)C{=}C{=}CHBr$ (**1e–g**) [a]

Entry	1	R^2	Organocopper agent "RCu"	Temp. (°C)	Time (h)	Conversion [b] (%)	Yield (%) [b]	
							8	**9**
1	**1f**	^{n}Pr	^{n}BuCu $MgBr_2$ (**2b**)	−70 to −40	1	29 [c]	7	93
2	**1f**	^{n}Pr	$^n Bu_2CuMgBr$ (**3b**)	−70 to −40	1	85	5	95
3 [d]	**1f**	^{n}Pr	CuBr 5%-^{n}BuMgBr (**4b**)	−70 to −40	1	100	23	77(58)
4	**1e**	Et	$^n Bu_2CuLi$ (**5b**)	−60	1	100	0	100(83)
5	**1e**	Et	$^i Bu_2CuLi$ (**5d**)	−60	1	100	0	98(70)
6 [e]	**1g**	^{t}Bu	$^t Bu_2CuLi$ (**5f**)	−60	1	100	0	18
7	**1e**	Et	^{n}Bu(CN)CuLi (**6b**)	−70	1	100	91(74)	9
8	**1e**	Et	^{i}Bu(CN)CuLi (**6d**)	−70	1	97	46	54
9 [f]	**1g**	^{t}Bu	^{t}Bu(CN)CuLi (**6f**)	−70	1	100	0	52
10	**1e**	Et	(^{n}BuCuBr)MgBr·LiBr (**7b**)	−70	0.5	100	97(73)	3
11	**1e**	Et	(^{i}BuCuBr)MgBr·LiBr (**7d**)	−70	0.5	100	11	89(82)
12	**1g**	^{t}Bu	(^{t}BuCuBr)MgBr·LiBr (**7f**)	−70	0.5	100	0	100(88)

[a] Except as noted, all reactions were performed on a 10-mmol scale by treating the allenic substrate **1** with 2 equivalents of the organocopper reagent, in Et_2O or THF as solvent. [b] Determined by GLC analyses of the mixture after hydrolysis; isolated yields are shown in parentheses. [c] After 12 h the temperature rised to −10 °C and the conversion to 73%; ratio alkyne/allene = 5/95. [d] Molar ratios **1f**:CuBr:^{n}BuMgBr = 1:0.05:2. [e] The reaction mixture contained 37% of 3,4,4-trimethyl-1,2-pentadiene (**10**) and 22% of 2,2,3,8,9,9,-hexamethyl-3,4,5,6-decatetraene (**11**). [f] The reaction mixture contained substantial amounts of **10** (25%) and **11** (16%).

n-butylcyano- and n-butylbromocuprates selectively afford the acetylenic compounds **8** which were isolated in good yields by fractional distillation (entries 7 and 10), in the other cases the trisubstituted allenic hydrocarbon **9** was the main product.

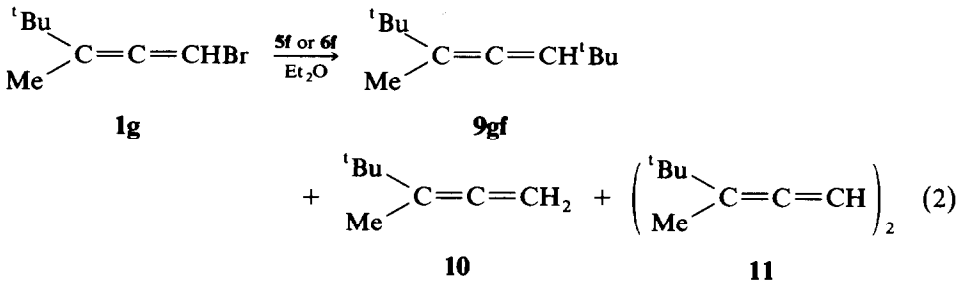
The data listed in Table 1 deserve some additional comments: (i) While the use of THF as solvent is critical for the reaction of the complex bromocuprates **7** (entries 10–12) the other copper reagents **2–6** can be used either in diethyl ether or tetrahydrofuran. In entries 1–9 we show the results obtained for coupling reactions in diethyl ether; however, when the THF was used in place of diethyl ether there was no substantial change in product distribution. For example, the reaction of **1f** with n-BuMgBr and catalytic amounts of CuBr give **9fb** in 87% yield together with 13% of **8fb** (see entry 3). Analogously, from **1e** and n-Bu_2CuLi in THF, the allenic hydrocarbon **9eb** was isolated in 71% yield (see entry 4). Finally, when the reaction indicated in entry 7 was carried out in THF the product mixture contained 87% of **8eb** and 11% **9eb**. (ii) In accord with Landor's observations [6] and with our results when using Ph_2CuLi [2d], the lithium dibutylcuprates **5b–f** react with bromoallenes to give exclusively the allenic products **9** (entries 4–6). (iii) In the reactions of $^t Bu_2CuLi$ (**5f**) and ^{t}Bu(CN)CuLi (**6f**) with 1-bromo-3,4,4-trimethyl-1,2-pentadiene (**1g**) **10** and **11** were formed, corresponding to reduction and dimerization of the allenic substrate (entries 6 and 9) (eq. 2). (iv) In contrast to our findings for coupling reactions involving Ph(CN)CuLi and (PhCuBr)MgBr · LiBr [2d], the alkylcyanocuprates **6b–f** and the corresponding bromocuprates **7b–f** show similar behaviour (entries 7–9 compared with entries 10–12). With these reagents the regioselectivity of the coupling process appears to be sensitive to steric factors (entries 7–12).

Table 2

Reaction of bromocuprates (RCuBr)MgBr·LiBr (7) with 3-alkyl-1-bromo-1,2-diene $R^2CH{=}C{=}CHBr$ (1a–d) [a]

Entry	1	R^2	7	R	Products 8, 9	Yields (%) [b]	
						8	9
13	1a	Me	7e	^{i}Pr	ae	92(68) [c]	8
14	1a	Me	7f	^{t}Bu	af	9	91
15	1b	Et	7b	^{n}Bu	bb	92	8
16	1b	Et	7c	$^{n}C_7H_{15}$	bc	93(79)	7
17	1b	Et	7d	^{i}Bu	bd	98(60) [c]	2
18	1b	Et	7e	^{i}Pr	be	82	18
19	1b	Et	7f	^{t}Bu	bf	8	92(76)
20	1c	^{i}Pr	7a	Et	ca	83(58) [c]	17
21	1c	^{i}Pr	7c	$^{n}C_7H_{15}$	cc	97(92)	3
22	1c	^{i}Pr	7d	^{i}Bu	cd	96(80)	4
23	1c	^{i}Pr	7e	^{i}Pr	ce	88	12
24	1c	^{i}Pr	7f	^{t}Bu	cf	0	100(98)
25	1d	^{t}Bu	7a	Et	da	95(65) [c]	5
26	1d	^{t}Bu	7d	^{i}Bu	dd	95(91)	5
27	1d	^{t}Bu	7e	^{i}Pr	de	35	65
28	1d	^{t}Bu	7f	^{t}Bu	df	0	100(70)

[a] Reactions were performed on a 10-mmol scale by treating 1a–d with 2 equivalents of the organocopper reagents, in THF at −70 °C for 30 min. [b] Determined by GLC analyses; isolated yields are shown in parentheses. [c] Isolated yield by preparative GLC.



In the light of the above informations we decided that a more detailed structure-reactivity study would be of value in order to define the usefulness and scope of the alkylheterocuprates for the synthesis of branched 1-alkynes **8**. Thus we undertook a more thorough investigation of the regioselectivity of the reaction of 3-substituted and 3,3-di-substituted 1-bromoallenes (**1**) with alkylbromocuprates **7** of various structures. The results are listed in Tables 2 and 3.

Close examination of the data shows that, in general, the organocopper species (RCuBr)MgBr · LiBr give the acetylenic product **8** when R is a normal group, and the substituted allene **9** when R is a tertiary group. Steric hindrance at C-3 of the bromoallenic substrate becomes a dominant factor in determining the products when secondary or α-branched primary copper reagents are used *.

* The cyanocuprates **6** gave similar results.

Table 3

Reactions of bromocuprates (RCuBr)MgBr·LiBr (7) with 3,3-dialkyl-1-bromo-1,2-dienes $R^2(Me)C{=}C{=}CHBr$ (**1e–g**) [a]

Entry	1	R^2	7	R	Products 8, 9	Yield (%) [b]	
						8	9
29	**1e**	Et	**7a**	Et	**ea**	97(80)	3
10	**1e**	Et	**7b**	^{n}Bu	**eb**	97(73)	3
30	**1e**	Et	**7c**	$^{n}C_7H_{15}$	**ec**	98(97)	2
11	**1e**	Et	**7d**	^{i}Bu	**ed**	11	89(82)
31	**1e**	Et	**7e**	^{i}Pr	**ee**	2	98
32	**1e**	Et	**7f**	^{t}Bu	**ef**	0	100(98)
33	**1f**	^{n}Pr	**7b**	^{n}Bu	**fb**	95(87)	5
34	**1g**	^{t}Bu	**7a**	Et	**ga**	74	26
35	**1g**	^{t}Bu	**7b**	^{n}Bu	**gb**	66(55) [c]	34
36	**1g**	^{t}Bu	**7d**	^{i}Bu	**gd**	0	100
12	**1g**	^{t}Bu	**7f**	^{t}Bu	**gf**	0	100(88)

[a] Reactions were performed on a 10-mmol scale by treating **1e–g** with 2 equivalents of the organocopper reagents in THF at −70 °C for 30 min. [b] By GLC analyses; isolated yields are shown in parentheses. [c] Isolated yield by preparative GLC.

It is evident that the relative steric interactions at the reaction sites determine the product distribution. However, the bulk of the alkyl substituent in the copper species appears to be the dominant factor, as can be deduced by comparing entry 19 with entry 25; in the two reactions the same alkyl groups (Et, ^{t}Bu) are involved. When the tert-butyl group is bonded to the copper atom, the allenic compound **9** is obtained in 92% yield, whereas the acetylenic hydrocarbon **8** is the main product (95%) when the substrate is 1-bromo-4,4-dimethyl-1,2-pentadiene (**1d**) (see also entry 32 vs entry 34).

From the synthetic point of view, the reaction between bromoallenes **1** and the bromocuprates **7** can give 1-alkynes **8** in good yields when an appropriate selection of the structure of both of the reactants is made. Significantly, terminal acetylenes having a quaternary carbon atom in the α position to the triple bond can be selectively obtained (Table 3).

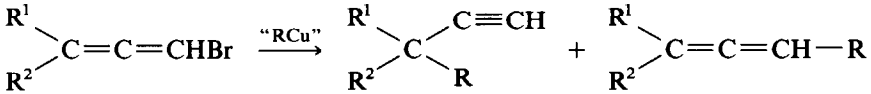
Subsequently, we studied the stereochemical outcome of the substitution reactions in order to establish further their synthetic value and to provide some mechanistic information. Such a study required chiral bromoallenes prepared from the corresponding optically active propargylic alcohols by stereospecific procedures described elsewhere [2e,10,11]. Thus, samples of optically active substrates, **1a** and **1e–g**, of known enantiomeric excess (ee) and absolute configuration [2e,10,11], were treated with various cuprates **5–7** under the conditions shown in Table 1; the results obtained are listed in Table 4.

The stereochemical characterization of the 1-alkynes **8ae** and **8fb**, obtained by using (*R*)-**1a** and (*R*)-**1f** as chiral substrates (entries 37–40), was based on chemical correlation with products of known stereochemistry [2e,12].

The absolute configuration of the allenes **9ed** and **9gf** (entries 41–45) was determined by preparing them via *anti* substitution reactions of the appropriate propargylic chiral substrates with cuprates **7d,f** [2b,13,14]. The *R* configuration for the levorotatory **9gf** (Scheme 2) is in full agreement with Vermeer's recent revision [13] of Corey's assignment [7] based on the Lowe–Brewster rules [15].

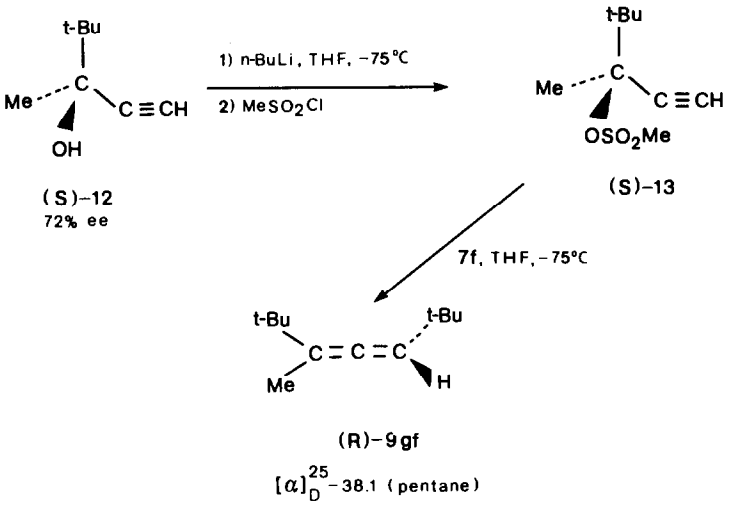
Table 4

Coupling reactions of organocuprates "RCu" with chiral substrates **1** [a]



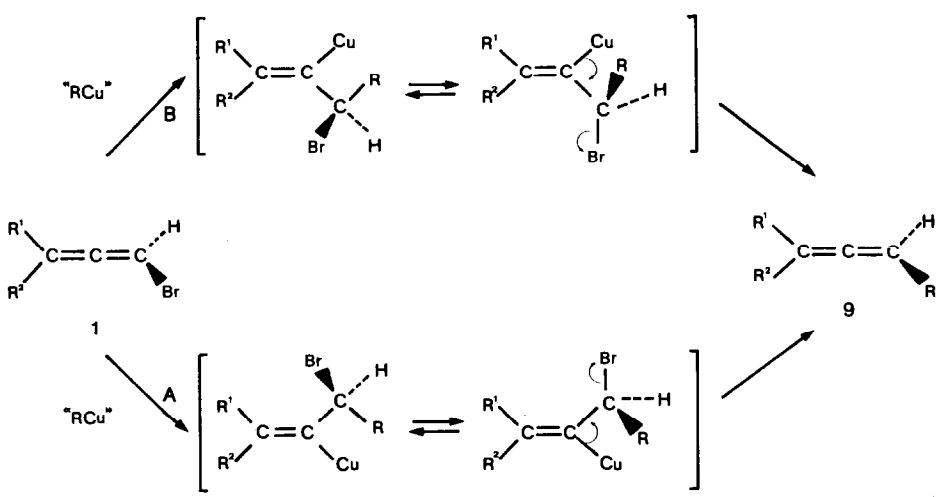
	1			**8**	**9**					
Entry	**1**			Organocopper agent "RCu"	Recovered product				Substitution process	Stereo-selectivity
		$[\alpha]_D^{25}$ [b]	ee%			yield% [c]	$[\alpha]_D^{25}$ [b]	ee%	config.		
37	(*R*)-**1a** [d]	−58.4 [e]	27	(^{i}PrCuBr)MgBr·LiBr	**8ae**	57	−7.51	25 [f]	*R* [f]	*anti*	96
38	(*R*)-**1f** [g]	−86.9	100	(^{n}BuCuBr)MgBr·LiBr	**8fb**	71	−2.49	99 [g]	*R* [g]	*anti*	> 99
39	(*R*)-**1f** [g]	−86.9	100	(^{n}BuCuBr)MgBr·LiBr	**8fb**	54	−2.40	96 [g]	*R* [g]	*anti*	98
40	(*R*)-**1f** [g]	−49.2	56	^{n}Bu(CN)CuLi	**8fb**	50	−1.42	56 [g]	*R* [g]	*anti*	> 99
41	(*S*)-**1e** [h]	+40.4	51	^{i}Bu$_2$CuLi	**9ed**	70	−4.80 [i]	18 [j]	*S* [k]	*anti*	68
42	(*S*)-**1e** [h]	+40.4	51	^{i}Bu(CN)CuLi	**9ed**	20	+9.62 [i]	33 [j]	*S* [k]	*syn*	83
43	(*S*)-**1e** [h]	+27.4	35	(^{i}BuCuBr)MgBr·LiBr	**9ed**	67	+8.38 [i]	31 [j]	*S* [k]	*syn*	95
44	(*R*)-**1g** [h]	−73.4 [l]	74	^{t}Bu(CN)CuLi	**9gf**	39	−31.78 [m]	54 [j]	*R* [n]	*syn*	87
45	(*S*)-**1g** [h]	+37.2 [l]	38	(^{t}BuCuBr)MgBr·LiBr	**9gf**	80	+14.33 [m]	24 [j]	*S* [n]	*syn*	82

[a] Reactions were carried out under the conditions indicated in Table 1. [b] Except as noted, rotations were measured on neat liquids. [c] Isolated yields by preparative GLC. [d] See ref. 11. [e] Abs. EtOH (*c* 6.5). [f] See ref. 12. [g] See ref. 2e. [h] See ref. 10. [i] hexane (*c* 7–10). [j] See ref. 16. [k] See ref. 2b. [l] at 20 °C. [m] pentane (*c* 1.5–4.0). [n] See ref. 13.

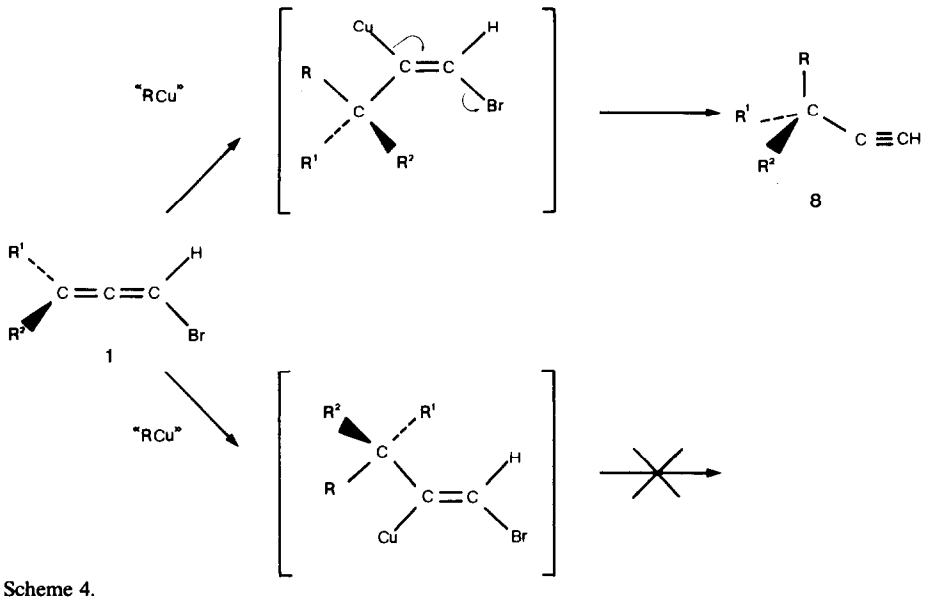


Scheme 2.

We determined the enantiomeric excess for **9ed** and **9gf** from the ^{195}Pt NMR spectra of the Pt complexes obtained by treating the chiral allenic hydrocarbons in chloroform at room temperature with an excess of *trans*-dichloro-[(*S*)-α-phenyl-ethylamine][ethylene]platinum (II) [16]. Examination of Table 4 reveals that the formation of 1-alkynes **8** from allenic bromides and alkylcyano- and alkylbromo-cuprates (**6** and **7**) proceeds in an highly *anti* stereochemical fashion (entries 37–40). This observation, which is consistent with our previous data for the formation of (*S*)-3-phenyl-1-butyne from (PhCuBr)MgBr · LiBr [2d] and with the Corey's results for the synthesis of chiral internal acetylenes [7], implies that our procedure provides a simple and convenient route to optically active alkynes and related compounds. It is noteworthy in this respect that the stereochemical results are highly reproducible (entries 38 and 39).



Scheme 3.



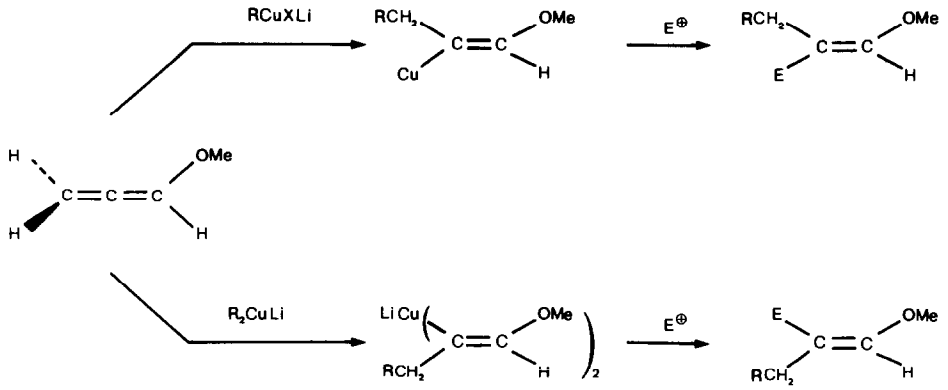
Scheme 4.

The results obtained for the reactions which selectively give the allenes **9** (entries 41–45) show that the direct substitution proceeds along two stereochemically opposite pathways, depending on the nature of the organocopper species. In particular, whereas the homocuprates give substituted allenes with predominant inversion of configuration (entry 41; see also ref. 5), the alkylcyano- and alkylbromo-cuprates give the allenic product with retention in the allenyl moiety (entries 42–45). The nature of the organocopper species seems also to affect the degree of stereoselectivity, but the possibility cannot be excluded that the racemization phenomena can be attributed to the contact of the allenic products with the excess of the cuprate during the reaction [17].

Although mechanistic interpretations of these data must be speculative, especially because of the undefined structure of the organocopper species actually involved, both the dynamic and stereochemical results seem to be consistent with the availability of alternative mechanisms for the reactions of bromoallenes **1** with copper reagents depending on the nature of the reagent.

The regioselectivity and the stereochemical outcome we have observed for the coupling between compounds **1** and the alkylheterocuprates **6** and **7** can be best rationalized in terms of addition–elimination routes (Scheme 3 and 4). The retention of configuration for the allenic products **9** would then originate from a *syn*-addition of the organocopper species to the C_1–C_2 double bond of the 1-bromo-1,2-diene followed by an *anti*-elimination (Scheme 3). It is noteworthy that the direction of attack (path A or B) does not affect the overall *syn* stereochemistry of the substitution process.

On the other hand, analogous addition–elimination steps involving the C_2–C_3 bond of **1** would account for the *anti*-stereoselectivity observed in 1-alkyne formation (Scheme 4). In this case, the attack of the copper reagent on the double bond from the side of the bromine atom could afford a vinylcopper intermediate which could not undergo the *anti*-elimination (Scheme 4) [18].

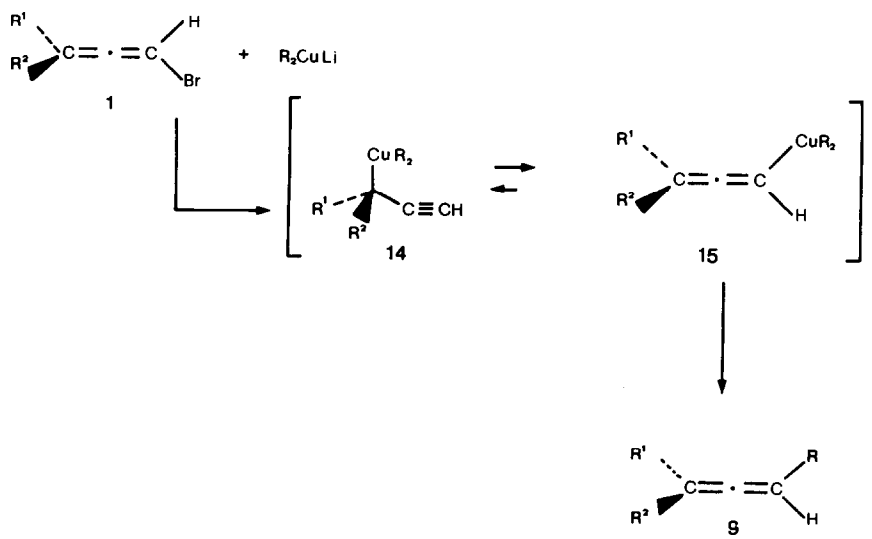


Scheme 5.

This scheme is consistent with the information reported by Alexakis and co-workers about the reactions of allenic ethers with different cuprates [19]. They reported that the addition of organocopper species to allenic ethers is highly dependent on the nature of the organometallic itself; lithium dialkylcuprates give *Z* vinylcopper species, whereas alkylheterocuprates give the corresponding *E* isomers (Scheme 5).

On this basis, the absence of acetylenic products when R_2CuLi are employed in our coupling reactions would be understandable. This mechanistic scheme we suggest can also account for the influence of the relative sizes of R, R^1 and R^2 groups on the regioselectivity of the copper-mediated displacement; in fact, as the bulk of these groups is increased the degree of preference for addition of the copper species to the C_1–C_2 bond of allenic substrate increases (see Tables 2 and 3).

This picture is different from that based on the results obtained in the reactions of lithium dialkylcuprates **5** with bromoallenes **1**, which in all cases give the allenic



Scheme 6.

hydrocarbons **9** [6] with inversion of configuration [5]. These results can be interpreted through a preferential displacement of bromide by nucleophilic copper in an *anti* sense, yielding the Cu^{III} intermediate **14** (Scheme 6) [7]. A suprafacial 1,3-shift of "R_2Cu" and subsequent 1,2-reductive elimination would give the allenic product with the observed *anti*-stereochemistry (Scheme 6). This different behaviour of R_2CuLi may be a consequence of the ate-complex structure of the reagent, in contrast with the neutral nature of the heterocuprates **6** and **7** [20]. The selective formation of allenes could be tentatively attributed to a higher stability of the σ-allenyl complex **15**, in view of what is known for palladium-catalyzed substitutions of allenic bromides and 2-propynyl-esters in reactions with organozinc reagents [21]. In these cases, also, only allenic and no acetylenic products are recovered. This mechanistic scheme is also similar to that proposed to account for cuprate displacements of propargylic leaving groups, which afford allenes with *anti*-stereoselectivity [14,22].

Experimental

IR spectra were recorded on a Perkin–Elmer FT-IR 1710 spectrophotometer as neat films. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer in $CDCl_3$ solution with Me_4Si as internal standard. Mass spectra were obtained with a VG-Analytical 7070 GC-MS instrument. Optical rotations were measured with a Perkin–Elmer 142 automatic polarimeter, using standard cuvettes ($l = 0.1$ and 1 dm). GLC analyses were performed on a Perkin–Elmer Model 5800 equipped with a flame ionization detector in a fused silica capillary column (BP1 bonded, 0.22 mm × 12 m). Preparative GLC (Perkin–Elmer F21 instrument) were performed with SE-30 and Carbowax 20M as stationary phases.

All solvents were reagent-grade materials, purified by standard methods, and redistilled under nitrogen from $LiAlH_4$ before use. n-Butyllithium (as a 1.6 *M* solution in hexane) and tert-butyllithium (as a 1.4 solution in pentane) were purchased from Fluka A.G.Co., Buchs. iso-Butyllithium was prepared in hexane by standard procedures. The molarities of the solutions were determined by Krieger's titration method [23]. Grignard reagents were prepared in Et_2O or THF and standardized by titration. Commercial (Fluka) lithium bromide, cuprous bromide, cuprous iodide, and cuprous cyanide were used without purification.

The racemic 1-bromo-1,2-dienes **1a–g** were made and purified as previously described (70–90% yield) [10,11,24], starting from the appropriate propargylic alcohols. (*R*)-1-Bromo-1,2-butadiene [(*R*)-**1a**] [11], (*S*)-1-bromo-3-methyl-1,2-pentadiene [(*S*)-**1e**] [10], (*R*)-1-bromo-3-methyl-1,2-hexadiene [(*R*)-**1f**] [2e], and (*R*)- and (*S*)-1-bromo-3,4,4-trimethyl-1,2-pentadiene, [(*R*)-**1g**] and [(*S*)-**1g**], [10] shown in Table 4 were prepared by published procedures starting from the corresponding optically active propargylic alcohols obtained by resolution methods [2e,25–27].

Homocuprates **5** were prepared by adding a solution of the required alkyllithium (20 mmol) dropwise to a stirred suspension of copper iodide (10 mmol) in diethyl ether at −60 °C [6]. Stirring was continued at −60 °C for 15 min and the mixture was then used immediately. Cyanocuprates **6** were prepared by treating a suspension of cuprous cyanide (10 mmol) in anhydrous diethyl ether (50 ml) at −30 °C with a stoichciometric amount of the alkyllithium compound [7]. The mixture was stirred at −30 °C for 30 min and the solution then used. Bromocuprates **7** were

Table 5

Spectral data for the alkynes **8**

Product	B.p. (°C/Torr)	^{1}H NMR ($CDCl_3$)/TMS) δ, J (Hz)	MS (70 eV) m/z (%)	IR (film) ν (cm^{-1})	Ref.
8ae	81/760	0.95 (d, 6H, CH_3); 1.11(d, 3H, CH_3); 1.36–1.78(m, 1H, CH); 1.92(d, 1H, J = 2.4, ≡CH); 2.05–2.50 (m, 1H, CHC≡)	96 (M^+, 4), 81 (97), 54 (100)	3312, 2112, 629	[12]
8af		0.95 (s, 9H, CH_3); 1.10 (d, 3H, CH_3); 1.93 (d, 1H, J = 2.2, ≡CH); 2.0–2.4 (m, 1H, CHC≡)	109 ($M^+ - 1$), 95 (40), 57 (100)		[12]
8bb		1.00 (2t, 6H, CH_3); 1.44 (m, 8H, CH_2); 2.01 (d, 1H, J = 2.5, ≡CH); 2.05–2.45 (m, 1H, CHC≡)	109 ($M^+ - CH_3$, 16) 95 (74), 67 (100)		[28]
8bc	94–96/15	0.88 (t, 3H, CH_3); 1.00 (t, 3H, CH_3); 1.15–1.70 (m, 14H, CH_2); 2.01 (d, 1H, J = 2.3, ≡CH); 2.10–2.40 (m, 1H, CHC≡)	138 ($M^+ - C_2H_5$, 7) 81 (68), 67 (100)		
8bd		0.88 (d, 3H, CH_3); 0.91 (d, 3H, CH_3); 1.0 (t, 3H, CH_3); 1.20–1.95 (m, 5H, CH_2, CH); 1.98 (d, 1H, J = 2.7, ≡CH); 2.32 (m, 1H, CHC≡)	123 ($M^+ - 1$, 1), 67 (91), 41 (100)	3313, 2114, 1467, 629	
8be/8ca	104/760	0.96 (d, 6H, CH_3); 1.0 (t, 3H, CH_3); 1.25–1.90 (m, 3H, CH, CH_2); 1.90–2.30 (m, 1H, CHC≡); 1.98 (d, 1H, J = 2.5, ≡CH)	110 (M^+, 1), 95 (60), 67 (100)		
8cc	98/16	0.88 (t, 3H, CH_3); 0.96 (d, 3H, CH_3); 0.98 (d, 3H, CH_3); 1.32 (m, 12H, CH_2); 1.44–1.85 (m, 1H, CH); 2.0 (d, 1H, J = 2.4, ≡CH); 2.18 (m, 1H, CHC≡)	165 ($M^+ - CH_3$, 1) 81 (100), 54 (61)	3312, 2105, 620	
8cd		0.79 (d, 3H, CH_3); 0.84 (d, 3H, CH_3); 0.86 (d, 3H, CH_3); 0.90 (d, 3H, CH_3); 1.20 (m, 2H, CH_2); 1.4–1.9 (m, 2H, CH); 1.87 (d, 1H, J = 2.5, ≡CH); 2.17 (m, 1H, CHC≡)	123 ($M^+ - CH_3$, 17), 95 (47), 81 (100), 43 (55)		
8ce		0.96 (d, 6H, CH_3); 0.99 (d, 6H, CH_3); 1.50–2.10 (m, 3H, CH, CHC≡); 2.02 (d, 1H, J = 2.01, ≡CH)	109 ($M^+ - CH_3$, 36) 82 (43),67 (100) 43 (55)		

Table 5 (continued)

Product	B.p. (°C/Torr)	^{1}H NMR ($CDCl_3$)/TMS) δ, J (Hz)	MS (70 eV) m/z (%)	IR (film) ν (cm^{-1})	Ref.
8bf/ **8da**		0.98 (s, 9H, CH_3); 1.03 (m, 3H, CH_3); 1.42 (m, 2H, CH_2); 1.75–2.07 (m, 1H, CHC≡); 2.00 (m, 1H, ≡CH)	109 ($M^+ - CH_3$, 14), 57 (100) 41 (27)		
8dd	63–64/17	0.87 (d, 3H, CH_3); 0.94 (d, 3H, CH_3); 1.25 (m, 2H, CH_2); 1.86 (m, 1H, CH); 2.01 (d, 1H, $J = 2.4$, ≡CH); 2.14 (m, 1H, CHC≡)	137 ($M^+ - CH_3$, 6), 109 (19), 57 (100)		
8de		2.05 (m, ≡CH)	138 (M^+, 3), 81 (23), 57 (100), 41 (32)		
8ea	101/760	0.97 (t, 6H, CH_3); 1.12 (s, 3H, CH_3); 1.43 (m, 4H, CH_2); 2.03 (s, 1H, ≡CH)	109 ($M^+ - 1$, 1); 95 (47), 81 (100); 79 (81)		[29]
8eb	49/16	0.92 (t, 3H, CH_3); 0.97 (t, 3H, CH_3); 1.13 (s, 3H, CH_3); 1.39 (m, 8H, CH_2), 2.05 (s, 1H, ≡CH)	137 ($M^+ - 1$), 81 (100), 67 (69)	3312, 2109, 628	
8ec	96/16	0.89 (t, 3H, CH_3); 0.97 (t, 3H, CH_3); 1.13 (s, 3H, CH_3); 1.32 (m, 14H, CH_2); 2.03 (s, 1H, ≡CH)	165 ($M^+ - CH_3$, 1), 95 (66), 81 (100)		
8ed		0.88–1.02 (m, 9H, CH_3); 1.15 (s, 3H, CH_3); 1.26–1.93 (m, 5H, CH_2, CH); 2.03 (s, 1H, ≡CH)	138 (M^+), 109 (54), 81 (88), 67 (94), 41 (100)	3300, 2100, 625	[2c]
8ee			109 ($M^+ - CH_3$, 21), 67 (100), 41 (52)		
8ga		0.98 (m, 12H, CH_3); 1.10 (s, 3H, CH_3); 1.37 (m, 2H, CH_2); 2.0 (s, 1H, ≡CH)	123 ($M^+ - CH_3$, 18), 67 (81), 57 (100), 41 (93)	3309, 2105, 629	[2c]
8gb	75/15	0.93 (t, 3H, CH_3); 1.0 (s, 9H, CH_3); 1.11 (s, 3H, CH_3); 1.38 (m, 6H, CH_2); 2.03 (s, 1H, ≡CH)	151 ($M^+ - CH_3$, 18), 68 (98), 57 (100)		
8fb	116/760	0.95 (m, 6H, CH_3); 1.15 (s, 3H, CH_3); 1.42 (m, 10H, CH_2); 2.05 (s, 1H, ≡CH)	151 ($M^+ - 1$), 109 (55), 95 (100), 81 (70), 67 (85)	3315, 2099, 619	[2e]

prepared by adding 1 molar equivalent of RMgBr at −50 °C to a well-stirred tetrahydofuran solution of $LiCuBr_2$ (20 mmol) made from stoicheiometric amounts of cuprous bromide and lithium bromide [9]. Stirring was continued at −50 °C for 30 min, and the mixture then used immediately.

Table 6

Spectral data for allenes **9**

Product	B.p. (°C/Torr)	^{1}H NMR ($CDCl_3$)/TMS) δ, J (Hz)	MS (70 eV) m/z (%)	IR (film) ν (cm^{-1})	Ref.
9af		0.9 (s, 9H, CH_3); 1.51 (dd, 3H, J = 4 and 6, CH_3C=); 4.92 (m, 2H, HC=C=CH)	110 (M^+, 28), 57 (100), 41 (40)		
9bb		5.10 (m, HC=C=CH)	109 ($M^+ - CH_3$, 1), 82 (78), 67 (100)		[30]
9bc		5.12 (m, HC=C=CH)	109 ($M^+ - C_4H_9$, 4), 82 (100), 67 (81)		
9bd		5.10 (m, HC=C=CH)	124 (M^+, 5), 67 (100), 41 (88)		[30b]
9be/ **9ca**		5.13 (m, HC=C=CH)	110 (M^+, 58), 95 (100), 81 (26)		
9cc		5.10 (m, HC=C=CH)	137 ($M^+ - C_3H_7$), 96 (89), 81 (100)		
9cd		5.10 (m, HC=C=CH)	138 (M^+, 5), 95 (100) 81 (96), 67 (75)		
9ce		5.13 (m, HC=C=CH)	124 (M^+, 43), 109 (78) 81 (55), 67 (100), 43 (58)		
9bf/ **9da**	62/50	1.00 (t, 3H, CH_3); 1.03 (s, 9H, CH_3); 1.97 (m, 2H, CH_2C=); 5.15 (m, 2H, HC=C=CH)	124 (M^+, 20), 109 (22), 57 (100), 41 (35),	1954	[14]
9dd		5.08 (m, HC=C=CH)	152 (M^+, 3), 95 (23), 57 (100)		
9cf/ **9de**	43/17	1.0 (d, 6H, CH_3); 1.05 (s, 9H, CH_3); 1.8–2.6 (m, 1H, CHC=); 5.13 (m, 2H, HC=C=CH)	138 (M^+, 15), 81 (24), 57 (100), 41 (30)	1960, 876	[14]
9df	48/17	1.03 (s, 18H, CH_3); 5.14 (s, 2H, HC=C=CH)	152 (M^+, 15), 137 (18), 81 (18), 57 (100), 41 (31)	1961, 878	[14]
9ea		0.98 (t, 6H, CH_3); 1.66 (d, 3H, J = 3, CH_3C=); 1.94 (m, 4H, CH_2C=); 5.10 (m, 1H, =C=CH)	110 (M^+, 58), 95 (52), 81 (86), 67 (100), 41 (89)		[6]
9eb	62/17	0.98 (m, 6H, CH_3); 1.33 (m, 4H, CH_2); 1.67 (d, 3H, J = 3, CH_3C=); 1.85 (m, 4H, CH_2C=); 5.00 (m, 1H, J = 3, =C=CH)	138 (M^+), 96 (70), 81 (100)	1960	[6]
9ec		5.02 (m, =C=CH)	151 ($M^+ - C_2H_5$), 96 (100), 81 (89)		
9ed	72/50	0.93 (d, 6H, CH_3); 0.98 (t, 3H, CH_3); 1.30–1.80 (m, 1H, CH); 1.65 (d, 3H, J = 3, CH_3C=); 1.83 (m, 4H, CH_2C=); 4.95 (m, 1H, =C=CH)	138 (M^+, 28), 109 (45), 96 (38), 81 (100), 67 (55), 41 (52)	1965	[2c]
9ee		0.97 (d, 6H, CH_3); 0.97 (t, 3H, CH_3); 1.67 (d, 3H, J = 3, CH_3C=); 1.60–2.50 (m, 3H, CH_2C=, CHC=); 5.03 (m, 1H, =C=CH)	124 (M^+, 84), 109 (57), 81 (86), 67 (100), 41 (68)		

Table 6 (continued)

Product	B.p. (°C/Torr)	^{1}H NMR ($CDCl_3$)/TMS δ, J (Hz)	MS (70 eV) m/z (%)	IR (film) ν (cm^{-1})	Ref.
9ef	112/760	0.97 (t, 3H, CH_3); 1.0 (s, 9H, CH_3); 1.67 (d, 3H, $J = 3$, CH_3C=); 1.92 (dq, 2H, CH_2C=); 4.97 (m, 1H, $J = 3$, =C=CH)	138 (M^+, 26), 123 (21), 81 (36), 67 (46), 57 (100), 41 (38)		
9fb	70/17	0.98 (m, 6H, CH_3); 1.30 (m, 6H, CH_2); 1.66 (d, 3H, $J = 3$, CH_3C=); 1.85 (m, 4H, CH_2C=); 4.99 (m, 1H, $J = 3$, =C=CH)	137 ($M^+ - 15$), 110 (60), 95 (69), 68 (22)		[2e]
9ga		0.96 (t, 3H, CH_3); 1.03 (s, 9H, CH_3); 1.66 (d, 3H, $J = 2.7$, CH_3C=); 1.93 (m, 2H, CH_2C=); 5.05 (m, 1H, =C=CH)	138 (M^+, 13), 81 (16), 67 (26), 57 (100), 41 (55)		[2c]
9gb		0.95 (t, 3H, CH_3); 1.04 (s, 9H, CH_3); 1.38 (m, 4H, CH_2); 1.66 (d, 3H, $J = 2.9$, CH_3C=); 1.98 (m, 2H, CH_2C=); 5.02 (m, 1H, =C=CH)	151 ($M^+ - CH_3$, 1), 124 (42), 109 (45), 57 (100)		[6]
9gd		0.92 (d, 6H, CH_3); 1.04 (s, 9H, CH_3); 1.30–1.80 (m, 1H, CH); 1.67 (d, 3H, $J = 3$, CH_3C=); 1.85 (m, 2H, CH_2C=); 4.95 (m, 1H, =C=CH)	166 (M^+, 9), 123 (15) 109 (43), 95 (47), 57 (100), 41 (95)	1965	[2c]
9gf	62–63/17	1.01 (s, 9H, CH_3); 1.04 (s, 9H, CH_3); 1.68 (d, 3H, $J = 2.8$, CH_3C=); 4.98 (q, 1H, $J = 2.8$, =C=CH)	166 (M^+, 10), 109 (18), 95 (22), 57 (100), 41 (16)	1962	[31]

Reaction of 1-bromo-1,2-dienes ***1a–g*** *with organocopper reagents. General procedure*

All reactions were carried out at least in duplicate, under a dry nitrogen atmosphere. In a typical experiment, a solution of 1-bromo-1,2-diene (**1**) (10 mmol) in tetrahydrofuran or diethyl ether (10 ml) was added, at −60 to −70 °C during 5 min to the cuprate reagent (20 equivalents) prepared by the procedures described. The progress of the reactions was monitored by GLC analysis until they were complete (Table 1). The mixture was then treated with saturated ammonium chloride (50 ml) and the organic materials were extracted with diethyl ether (3 × 50 ml). The combined extracts were washed with additional aqueous ammonium chloride (2 × 50 ml) and with water (50 ml), then dried (Na_2SO_4) and analyzed by GLC. Fractional distillation (Fischer–Spaltrohr MMS 202 column) or preparative GLC yielded pure products **8** and **9**. In some cases pure acetylenic compounds were obtained through the corresponding silver salts [12]. Spectral data for compounds **8** and **9** are listed in Tables 5 and 6 respectively.

*Reaction of 1-bromo-3,4,4-trimethyl-1,2-pentadiene (**1g**) with lithium di-tert-butylcuprate (**5f**) (entry 6)*

According to the general procedure, a solution of 32 mmol of tert-butyllithium in pentane was added at −60 °C to a stirred suspension of cuprous iodide (3 g, 16 mmol) in dry diethyl ether. Subsequently, the allenic bromide **1g** (3.0 g, 16 mmol) was added during 5 min, and stirring was continued, at −60 °C for 1 h. The usual work-up gave a mixture of 2,2,3,6,6-pentamethyl-3,4-heptadiene (**9gf**), 3,4,4-trimethyl-1,2-pentadiene (**10**), and 2,2,3,8,9,9-hexamethyl-3,4,6,7-decatetraene (**11**) which was separated by preparative GLC (SE-30).

9gf: (see Table 6). ^{13}C NMR: δ 15.4, 29.2, 30.3, 32.0, 33.2, 102.3, 109.7, 197.3.

10: MS (*m/z*): 110 (21%, M^+), 95 (21), 67 (19), 57 (100), 55 (19), 41 (51). ^{1}H NMR: δ 1.05 (s, 9H, CH_3); 1.68 (t, 3H, J = 3 Hz, =CCH_3); 4.57 (q, 2H, J = 3 Hz, =C=CH_2).

11: MS (*m/z*): 218 (11%, M^+), 203 (3), 161 (7), 147 (10), 119 (12), 105 (21), 91 (12), 77 (9), 57 (100), 41 (25). ^{1}H NMR: δ 1.05 (s, 18H, CH_3); 1.70 (m, 6H, =CCH_3); 5.46 (m, 2H, =C=CH). ^{13}C NMR: δ 14.96, 15.07, 29.21, 29.25, 33.83, 33.90, 90.57, 90.84, 110.29, 110.40, 202.89, 202.95.

*Preparation of (−)-(R)-2,2,3,6,6-pentamethyl-3,4-heptadiene [(R)-**9gf**] from mesylate (S)-**13***

A solution of (*S*)-3,4,4-trimethyl-1-pentyn-3-ol [(*S*)-**12**] (3.15 g, 25 mmol), $[\alpha]_D^{25}$ +0.81 [10b,25] in anhydrous THF (70 ml) was treated at −75 °C with a stoicheiometric amount of butyllithium 1.6 *M* in hexane. Subsequently, at the same temperature, were added 2.9 g (25 mmol) of methanesulfonyl chloride. After 10 min the mixture was added at −75 °C via a cannula to a well-stirred suspension of the bromocuprate **7f** (50 mmol), prepared in THF (100 ml) by the procedure described above. Stirring was continued at −75 °C for 2 h, then the mixture was hydrolyzed with aqueous ammonium chloride. After the usual work-up, careful distillation gave pure (*R*)-**9gf** (3.3 g, 79% yield) having b.p. 62 °C/17 Torr; $[\alpha]_D^{25}$ −38.1 (pentane, *c* 1.6) (See Table 6 for characteristic spectroscopic data).

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