Synthesis of Allenes by 1,6-Addition of Organocuprates to Polarized Enynes

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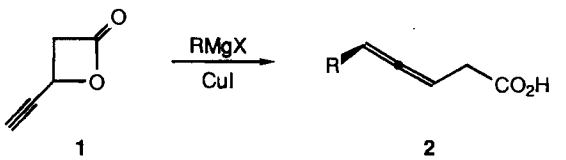
Ten β-allenic esters, ketones, and thioesters **15** bearing alkyl, alkenyl, aryl, and trimethylsilyl groups are synthesized in 57–85% yield by 1,6-addition of organocuprates to polarized enynes **10**. The dependence of the regioselectivity of the protonation of the allenyl enolate intermediate **7** on the protonating agent is studied; pure allenes are obtained by quenching the intermediate with pivalic acid at −80°C. The method is applied in a short synthesis of pseudoionone (**18**).

Allenes play an important role in organic chemistry, due to their unique structural features that make them intriguing both from a theoretical and a synthetic point of view[1–6]. Several natural products contain the allene moiety[1,2], making allenes themselves interesting target molecules. The conversion of allenes into other molecules ist the second important branch of allene chemistry; due to their high reactivity, reactions like cyclizations, metalation, and double bond isomerization can be achieved readily[1,4,5]. Unsymmetrically substituted allenes are chiral, and the synthesis and reactions of chiral, non-racemic allenes is a very modern field of allene chemistry[1,6]. There is a plethora of methods for the synthesis of allenes[1,3,7], but many of these can only be employed for the preparation of simple alkyl- and aryl-substituted allenes. The number of general schemes for the synthesis of allenes bearing three or four different and/or structurally complex substituents is rather small. With this background and in connection with the continuing work on mechanisms and synthetic applications of organocuprate reactions[8,9], it seemed interesting to examine the possibilities for the preparation of allenes by 1,6-addition of cuprates to polarized enynes.

Conjugate 1,4-additions of organocuprates to enones and enoates are fundamental in modern organic chemistry[8]. Likewise, 1,6-additions of cuprates to 2,4-dienoates can be achieved, with regioselectivity that depends on the nature of the cuprate as well as on the reaction conditions[10]. In contrast to this, only two cases of 1,6-addition reactions of organocuprates to polarized enynes have been reported so far. Thus, the β-lactone **1** reacts with Grignard reagents under catalysis with copper(I) iodide, yielding 3,4-dienoic acids **2**[11]. Similarly, the cyclic ketone **3** undergoes 1,6-addition with cuprates; however, protonation gives rise to the formation of 2,4-dienones[12].



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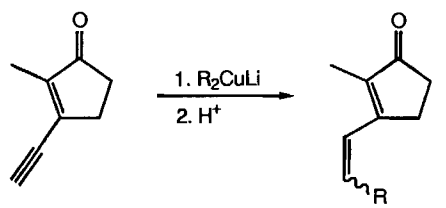

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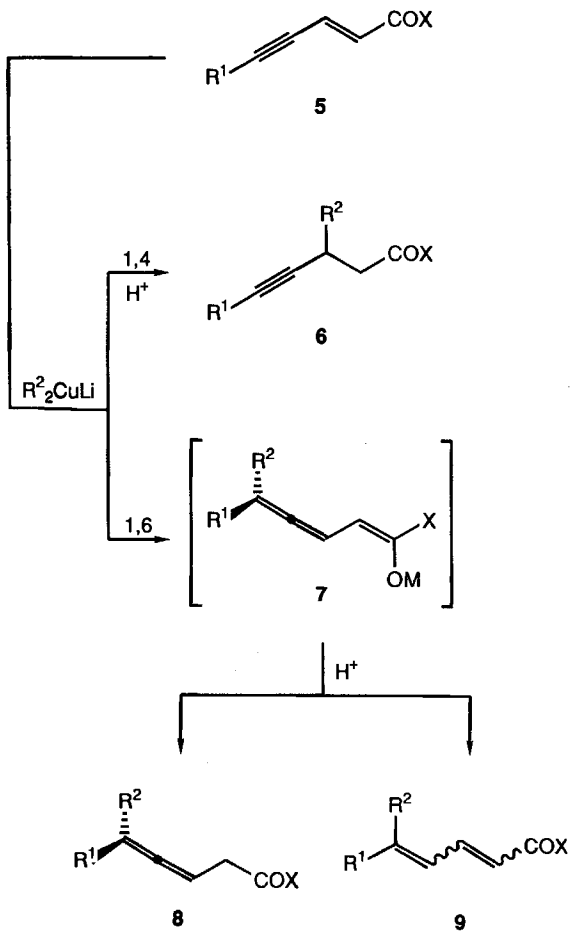

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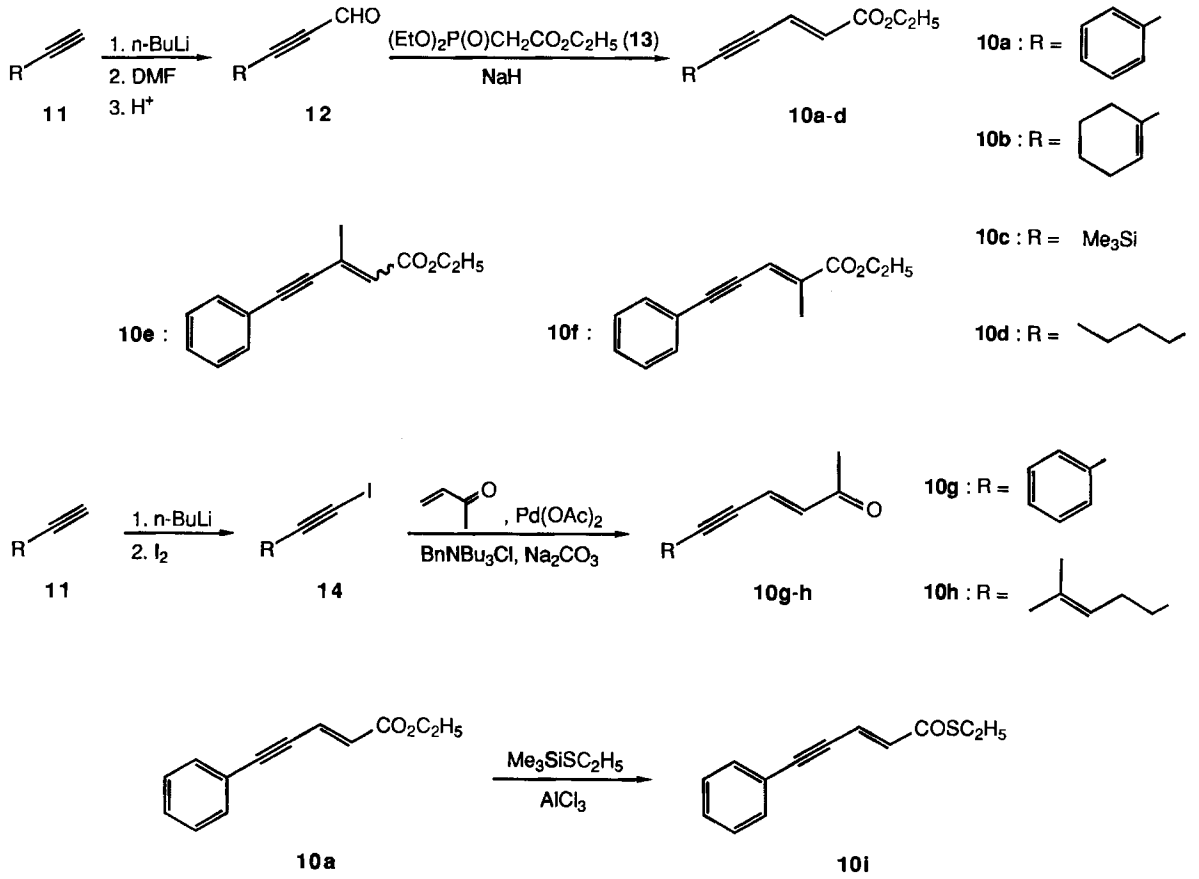
The result of a cuprate addition to a polarized enyne **5** depends on two problems of regioselectivity. First, the cuprate may add in a 1,4- (→ **6**) or a 1,6- fashion (→ **7**). If the latter is occurring, protonation of the allenyl enolate intermediate **7** can take place in 2-position (→ allenes **8**) or in 4-position (→ dienes **9**). During the workup of the reaction mixture it is important to avoid basic conditions since β-allenic ketones and esters are known to isomerize readily in basic media to the thermodynamically preferred 2,4-dienones and 2,4-dienoates[13].

1. Preparative Results

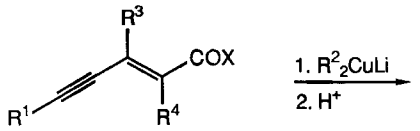
The starting materials for the addition experiments, the polarized enynes **10**, are readily accessible by standard methods. Thus, the esters **10a–d**[14,15] were obtained from terminal acetylenes **11** by formation of the aldehydes **12**[16a], followed by Wittig-Horner olefination with the phosphonate **13**. The known methylated esters **10e**[17] and **10f**[18] were synthesized similarly. The ketones **10g,h** were prepared via the acetylenic iodides **14**[16b] by palladium-catalyzed coupling with 3-buten-2-one[19]. Ester **10a** was converted into thioester **10i** by treatment with (ethylthio)trimethylsilane and aluminium trichloride[20].

The first addition experiment, carried out with enynoate **10a** and lithium dimethylcuprate in diethyl ether as solvent, showed exclusively 1,6-addition of the cuprate to the enyne (Table 1, entry 1). The reaction was complete in 1 h at −20 °C; after hydrolysis with 2 N H_2SO_4 (workup procedure A) the allene **15a** was isolated in 79% yield, and no dienes **16a** could be detected by ^{1}H-NMR spectroscopy. The color changes of the mixture during the reaction served as indicator for the progress of the reaction. If the enynoate is added to the colorless cuprate solution, a brilliant red solution is formed; this also happens below −50 °C, i.e. under conditions where no addition of the cuprate to the enyne is taking place. Therefore, the red color is probably due to a loose interaction of the π system of the enynoate with copper atom(s) fixed in the cuprate cluster. As the reaction proceeds, a yellow precipitate is formed; this probably consists of insoluble methylcopper since separation of the supernatant solution and hydrolysis gives allene **15a** without the formation of copper salts. Thus, the adduct of lithium dimethylcuprate to ester **10a** seems to exist as a lithium allenyl enolate; however, this may be different for other cuprates used in this work (see below).

Similarly to **15a**, cyclohexenyl- and trimethylsilyl-substituted allenes **15b** and **15c** were obtained from enynoates **10b/c** and Me_2CuLi (entries 2 and 3); thus, this method opens another route to the particularly useful silylallenes[5]. In contrast to this, application of the same reaction conditions to the alkyl-substituted enynoate **10d** led to the formation of a 9:1 mixture of allene **15d** and dienes **16d** (entry 4). This problem was also encountered with ester **10a** and *n*-Bu_2CuLi (entry 6) and with ester **10f** and Me_2CuLi (entry 15). In the latter case a disappointingly low allene:diene ratio of 1:1 was observed. Thus, the regioselectivity of the protonation of the intermediate **7** appears to be a function



of the substitution pattern of the starting enyne as well as the nature of the organocuprate employed.



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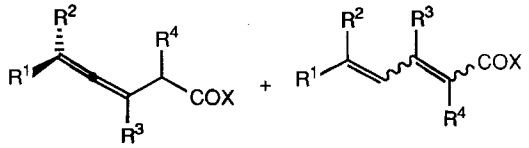


15 16

Table 1. Preparation of allenes $R^1R^2C=C=CR^3CHR^4COX$ **15** by 1,6-addition of organocuprates to enynes **10**

Entry	Enyne	Cuprate	Allene	R^1	R^2	R^3	R^4	X	Workup[b]	Yield	**15** : **16**[c]
1	**10a**	Me_2CuLi	**15a**	Ph	Me	H	H	OEt	A	79%	>99 : <1
2	**10b**	Me_2CuLi	**15b**	Cyclohexenyl	Me	H	H	OEt	A	75%	>99 : <1
3	**10c**	Me_2CuLi	**15c**	Me_3Si	Me	H	H	OEt	A	57%	>99 : <1
4	**10d**	Me_2CuLi	**15d**	n-Bu	Me	H	H	OEt	A	85%	9 : 1
5	**10d**	Me_2CuLi	**15d**	n-Bu	Me	H	H	OEt	B	71%	>99 : <1
6	**10a**	$n\text{-}Bu_2CuLi$	**15e**	Ph	n-Bu	H	H	OEt	A	57%	4 : 1
7	**10a**	$n\text{-}BuCu(C{\equiv}CBu)Li$	**15e**	Ph	n-Bu	H	H	OEt	A	52%	4 : 1
8	**10a**	$n\text{-}Bu_2Cu(CN)Li_2$	**15e**	Ph	n-Bu	H	H	OEt	A	61%	4 : 1
9	**10a**	$n\text{-}Bu_2Cu(CN)Li_2$	**15e**	Ph	n-Bu	H	H	OEt	B	70%	>99 : <1
10	**10a**	$n\text{-}BuCu(CN)Li$	**15e**	Ph	n-Bu	H	H	OEt	B	0%[d]	-
11	**10a**	$n\text{-}BuCu{\cdot}BF_3$	**15e**	Ph	n-Bu	H	H	OEt	A	0%[d]	-
12	**10d**	Ph_2CuLi	**15e**	n-Bu	Ph	H	H	OEt	A	62%	>99 : <1
13	**10a**	$t\text{-}Bu_2Cu(CN)Li_2$	**15f**	Ph	t-Bu	H	H	OEt	A	81%	>99 : <1
14	**10e**	Me_2CuLi	**15g**	Ph	Me	Me	H	OEt	B	75%	>99 : <1
15	**10f**	Me_2CuLi	**15h**	Ph	Me	H	Me	OEt	A	69%	1 : 1
16	**10f**	Me_2CuLi	**15h**	Ph	Me	H	Me	OEt	B	62%	>99 : <1
17	**10g**	$t\text{-}Bu_2Cu(CN)Li_2$	**15i**	Ph	t-Bu	H	H	Me	A[e]	65%	20 : 1
18	**10i**	Me_2CuLi	**15j**	Ph	Me	H	H	SEt	B	65%	>99 : <1

[a] Reactions carried out at −20°C for 1 h in diethyl ether as solvent. — [b] Workup procedure A: 2 N H_2SO_4, 25°C; procedure B: pivalic acid, −80°C; cf. Experimental. — [c] Determined by ^{1}H-NMR spectroscopy; a ratio of >99 : <1 is given if no dienes **16** could be detected. — [d] Only polymeric products were obtained besides unreacted starting material. — [e] Workup with 0.1 N H_2SO_4 at 0°C.

In order to gain a better insight into the influence of the protonating agent on the regioselectivity of the protonation of **7**, the adduct of lithium dimethylcuprate to ester **10f** was treated with different acids; the results are summarized in Table 2. Strong acids in protic and aprotic solvents, i.e. sulfuric acid, *p*-toluenesulfonic acid, and trichloroacetic acid, almost invariably gave allene:diene ratios close to 1:1 (entries 1–7). In these cases, the influences of temperature (entries 2 and 6 vs. **1** and 5) and acid concentration (entry 3 vs. 1) seem to be negligible. Similar results were obtained with citric and lactic acid (entries 8 and 9). A small improvement of the ratio of **15h**:**16h** up to 2.4:1 could be achieved by using moderately strong organic acids like acetic acid, benzoic acid, and diphenylacetic acid in diethyl ether as solvent (entries 10–13). The relatively high ratio observed with diphenylacetic acid (2.4:1) compared to that of the similar strong benzoic acid (1.3:1) gives rise to the assumption that the regioselectivity of the protonation of the cuprate adduct to **10f** might be controlled not only by the strength but also by the steric demand of the protonating agent[21]. Accordingly, use of the bulky pivalic acid produced a ratio of **15h**:**16h** = 4.7:1 at 25°C (entry 14). If the protonation is carried out at −80°C, the desired allene **15h** is the sole product (entry 15) and can be isolated in 62% yield as a 1:1 mixture of diastereomers (Table 1, entry 16)! Thus, pivalic acid represents the perfect balance between acid strength and bulkiness for the regioselective protonation of the Me_2CuLi adduct to ester **10f**.

Table 2. Protonation of the Me_2CuLi adduct to **10f** with different acids[a]

Entry	Acid	Solvent	Temperature	**15h** : **16h**	pK_a[b]
1	2 N Sulfuric acid	Water	25°C	1 : 1	
2	2 N Sulfuric acid	Water	0°C	1 : 1.2	
3	0.1 N Sulfuric acid	Water	25°C	1 : 1.6	
4	2 N Sulfuric acid[c]	Water	25°C	1 : 1.4	
5	p-Toluenesulfonic acid	Methanol	25°C	1 : 1	
6	p-Toluenesulfonic acid	Methanol	-80°C	1 : 1.4	
7	Trichloroacetic acid	Diethyl ether	25°C	1 : 1.4	0.66
8	Citric acid	Methanol	25°C	1 : 1.7	3.22
9	Lactic acid	Diethyl ether	25°C	1 : 1	3.86
10	Acetic acid	Hexane	25°C	1.3 : 1	4.76
11	Acetic acid	Diethyl ether	25°C	1.8 : 1	4.76
12	Benzoic acid	Diethyl ether	25°C	1.3 : 1	4.20
13	Diphenylacetic acid	Diethyl ether	25°C	2.4 : 1	3.94
14	Pivalic acid	Diethyl ether	25°C	4.7 : 1	5.03
15	Pivalic acid	Diethyl ether	-80°C	>99 : <1[d]	5.03

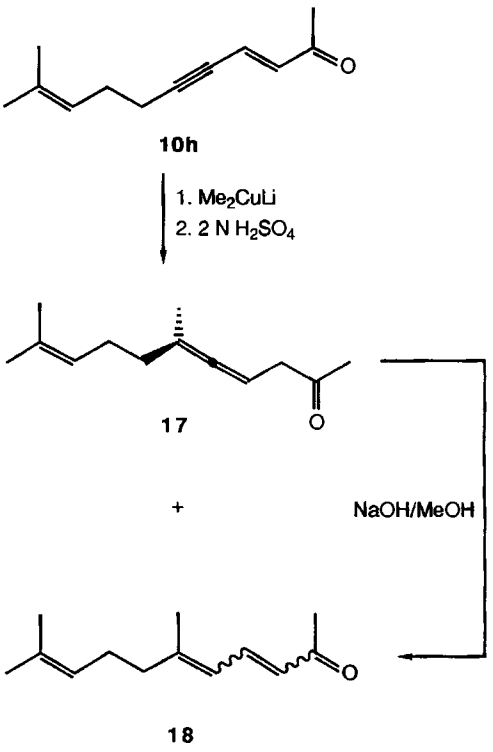
[a] Preparation of the Me_2CuLi adduct to **10f** according to the General Procedure; the ratio of **15h**:**16h** was determined by ^{1}H-NMR spectroscopy. — [b] Ref.[22]. — [c] After removal of the precipitation. — [d] No dienes **16h** could be detected.

The regioselective protonation of the allenyl enolate intermediate with pivalic acid at −80°C (workup procedure B) proved to be useful in other problematic cases as well. Thus, pure allene **15d** was obtained in 71% yield by 1,6-addition of lithium dimethylcuprate to ester **10d** (Table 1, entry 5). For the transfer of an *n*-butyl group to enynoate **10a** different cuprates were examined. Here, the homocuprate $n\text{-}Bu_2CuLi$, the heterocuprate $n\text{-}BuCu(C{\equiv}CBu)Li$[23], and the copper(I) cyanide derived cuprate $n\text{-}Bu_2Cu(CN)Li_2$[8c] all gave 1,6-addition; after workup with 2 N H_2SO_4 a 4:1 mixture of allene **15e** and dienes **16e** was obtained in 52–61% yield (entries 6–8). In contrast to this, cuprates with a 1:1 stoichiometry of alkyllithium reagent and copper(I) salt, i.e. $n\text{-}BuCu(CN)Li$[8c] and $n\text{-}BuCu{\cdot}BF_3$[8b], did not react with ester **10a** (entries 10 and 11). With $n\text{-}Bu_2Cu(CN)Li_2$ [which is thermally more stable than the copper(I) iodide-derived $n\text{-}Bu_2CuLi$] and workup procedure B, pure allene **15e** was isolated in 70% yield (entry 9). The same product was obtained by reversal of R^1 and R^2, i.e. by addition of lithium diphenylcuprate to butyl-substituted en-

ynoate **10d**; surprisingly, workup with 2 N H_2SO_4 gave pure allene **15e**, and no dienes **16e** could be detected by ^{1}H-NMR spectroscopy (entry 12)! Thus, the allenyl enolates derived from **10a** + *n*-Bu_2CuLi and from **10d** and Ph_2CuLi behave differently during protonation. The sterically demanding *tert*-butyl group can also be introduced into allenes by this method; treatment of enynoate **10a** with *t*-$Bu_2Cu(CN)Li_2$ and workup with 2 N H_2SO_4 yielded pure allene **15f** in 81% yield (entry 13). Obviously, with bulky groups in 5-position, the protonation of intermediate **7** in 4-position to give dienes is strongly disfavored. The preparation of allenes with four substituents is feasible as well; 1,6-addition of lithium dimethylcuprate to ester **10e** and protonation with pivalic acid at −80°C afforded allene **15g** in 75% yield (entry 14).

This method is not restricted to the enynoates but may be applied to enynes polarized by keto and thioester groups as well. With 2-en-4-ynone **10g** as substrate 1,6-addition takes place exclusively, though the protonation of the formed allenyl enolate is not as regioselective as with enynoates. Thus, addition of Me_2CuLi to **10g** and workup with 2 N H_2SO_4 yields a 1:1 mixture of allene and dienes. This ratio is *not* altered significantly if the protonation is carried out with pivalic acid at −80°C. In contrast to enynoate **10f**, the regioselectivity of the protonation of the Me_2CuLi adduct to ketone **10g** is improved to 3:1 by quenching with 0.1 N H_2SO_4 at 0°C. Preparatively useful ratios are achieved if the bulky *tert*-butyl group is transferred. By addition of *t*-$Bu_2Cu(CN)Li_2$ to **10g** and workup with 0.1 N H_2SO_4 at 0°C allene **15i** was obtained in 65% yield with a ratio of **15i**:**16i** = 20:1 (Table 1, entry 17). The reactivity of thioester **10i** is similar to that of the esters examined in this work; lithium dimethylcuprate adds in a 1,6-fashion exclusively, and protonation with pivalic acid at −80°C provides allene **15j** in 65% yield without detectable diene impurities (entry 18). The well-known substitution of thiolate by the organocuprate[24] does not compete with the 1,6-addition reaction. The method meets its limitations when enynes with other, less polarizing groups X are used. If the ester group in **10a** is replaced by nitrile or diethylamide, reaction with lithium dimethylcuprate no longer takes place anymore. In the case of the aldehyde, the starting material is consumed, but protonation with 2 N H_2SO_4 only gives rise to polymeric products. The method is limited with regard to the cuprate as well. Thus, ester **10a** reacts with the silyl cuprate $(Me_3Si)_2CuLi$[25] in a 1,4-fashion to yield ethyl 5-phenyl-3-(trimethylsilyl)-4-pentynoate. This finding is not surprising since it is well established that the chemical reactivity of silyl cuprates differs considerably from that of carbon cuprates[25]. As found in many other cases[26], the reaction is also strongly dependent on the structure of the cuprate cluster as influenced by the solvent. If THF is used instead of diethyl ether, no addition of *n*-Bu_2CuLi to enynoate **10a** occurs. Finally, the Me_2CuLi adduct to ester **10a** was treated with different electrophiles. Whereas methyl iodide did not react, allyl bromide and iodine afforded substituted 2,4-dienoic esters of type **9** by attack of the electrophile at the 4-position of allenyl enolate **7**. In contrast to this, treatment of the adduct with Me_3SiCl/HMPA furnished an *E*/*Z* mixture of the silylated allenyl ketene acetal (M = $SiMe_3$ in **7**). Further work is in progress in order to establish the synthetic use of these preliminary results.

Besides for the synthesis of β-allenic carbonyl compounds, the 1,6-addition of organocuprates to polarized enynes can also be useful for the preparation of 2,4-dienoates and 2,4-dienones with a deliberate substitution pattern since the latter are obtained readily from the allenes by base-catalyzed double bond isomerization[1,13]. In this case, of course, the regioselectivity of the protonation of the allenyl enolate **7** is not relevant. To give one example, enynone **10h** was treated with lithium dimethylcuprate, and after quenching with 2 N H_2SO_4 a 1:2 mixture of allene **17** and dienes **18** (pseudoionone) was isolated. Pure pseudoionone as a mixture of 3,5-*E*/*Z* isomers was obtained in 48% yield by treatment of the crude mixture of **17** and **18** with methanolic sodium hydroxide[27]. The advantage of this method is that by simple variation of the cuprate, analogs of **18** bearing different substituents in the 6-position should be accessible from a common starting material **10h**.



2. Discussion

In this work it has been shown that the two problems of regioselectivity mentioned in the introduction can be controlled in order to obtain pure β-allenic carbonyl compounds **15** by (i) regioselective 1,6-addition of organocuprates to polarized enynes **10** and (ii) regioselective protonation of the allenyl enolate intermediate **7**. Remarkably, the dependence of the 1,6-addition reaction on structural changes of the cuprate and the enyne is rather small, making the method fairly general. The reactivity of organocuprates towards the polarized enynes differs considerably from that of simple, non-organometallic nucleophiles such as amines,

thiolates, and sodium azide, which react with enynes of type **10** to give products of 1,2-addition to the double or the triple bond[28]. The high affinity of cuprates for acetylenes is reflected in their 1,4-addition reactions with acetylenic and α,β-unsaturated esters: The addition to acetylenic esters is fast even at −100°C[9a,29], whereas the addition to α,β-unsaturated esters does not occur below −30°C[26f,30]. Whether this affinity is due to an interaction of filled d orbitals of the copper atom(s) with the LUMO of the acetylenic substrate as proposed by Corey[31] is not settled at present; it seems necessary to include the complex structural features of the cuprate cluster[32] (which are very sensitive to the solvent and the presence of lithium salts[9a,26]) as well as the charge densities and HOMO/LUMO coefficients of the enyne (which are influenced by the polarizing group X) into mechanistic considerations in order to gain a more complete picture of the 1,6-addition reaction.

The second problem of regioselectivity, the protonation of the allenyl enolate **7**, appears to be controlled by several different parameters too. The steric influence of the protonating agent is obvious. With bulky acids like pivalic acid protonation at C-4 is disfavored, and pure β-allenic esters are obtained. However, acid strength, solvent, and temperature also influence the regioselectivity of the protonation, and this becomes more important if the polarizing group X is a keto group. Once again, it seems important to get more information about the steric and electronic properties of **7**, such as the charge distribution, in order to gain a better insight into the factors that are controlling the protonation. Nevertheless, although mechanistic details are lacking, the 1,6-addition of organocuprates to polarized enynes provides a versatile access to β-allenic carbonyl compounds with a complex substitution pattern, a fact that should allow the use of this method for the synthesis of structurally complex natural and unnatural allenes as well as target molecules derived from them.

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Experimental

IR: Perkin-Elmer IR spectrometer 197. – ^{1}H-, ^{13}C-NMR: Bruker WM-300 with $CDCl_3$ as solvent and internal standard (δ = 7.27 [^{1}H-NMR], δ = 77.05 [^{13}C-NMR]). Abbreviations for the DEPT spectra: + = CH_3, CH; − = CH_2; x = C(quart.). – Mass spectra: Varian MAT 311 A.

All reactions were carried out in thoroughly dried glassware under nitrogen. Diethyl ether and THF were distilled from $LiAlH_4$ and potassium/benzophenone, respectively, prior to use. All other reagents were used without further purification.

Ethyl 5-Phenyl-2-penten-4-ynoate (**10a**): 1.8 g (60 mmol) of sodium hydride (80% in paraffin oil) was washed with pentane and suspended in 60 ml of THF. A solution of 13.5 g (60 mmol) of **13** in 60 ml of THF was added dropwise with stirring at room temperature. After evolution of hydrogen gas had stopped (ca. 30 min) the mixture was cooled to 0°C, and a solution of 7.2 g (55 mmol) of 3-phenylpropinal (**12a**[16a]) in 30 ml of THF was added dropwise. The mixture was stirred at room temp. for 1 h and hydrolyzed and acidified with 2 N H_2SO_4. The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with water and dried with $MgSO_4$; the solvent was removed in vacuo. The crude product was chromatographed through a short column of silica gel (diethyl ether/hexane = 1:20) and purified further by kugelrohr distillation (110–120°C/0.001 Torr); yield 10.0 g (91%) **10a** as a colorless liquid which crystallized upon cooling. M. p. 23°C (hexane). – IR: $\tilde{\nu}$ = 2200 (s, C≡C), 1720 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.32 (t, 3H, *J* = 7.1 Hz, CH_3), 4.25 (q, 2H, *J* = 7.1 Hz, CH_2), 6.31 (d, 1H, *J* = 15.8 Hz, 2-H), 6.99 (d, 1H, *J* = 15.8 Hz, 3-H), 7.35–7.38 (m, 3H, phenyl-H), 7.47–7.50 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 14.2 (+, CH_3), 60.8 (−, CH_2), 86.4 (×, C-4/C-5), 98.2 (×, C-4/C-5), 122.3 (×, phenyl), 125.0 (+), 128.5 (+), 129.3 (+), 130.2 (+), 132.0 (+, C-2/C-3/phenyl), 165.9 (×, C-1). – MS: *m/z* (%) = 200 (62) [M^+], 127 (100).

$C_{13}H_{12}O_2$ (200.2) Calcd. C 77.98 H 6.04
Found C 77.88 H 5.91

Ethyl 5-(1-Cyclohexen-1-yl)-2-penten-4-ynoate (**10b**): The preparation was carried out as for **10a**, starting from 0.75 g (25 mmol) of sodium hydride, 5.61 g (25 mmol) of **13**, and 3.00 g (22 mmol) of 3-(1-cyclohexen-1-yl)propinal (**12b**[16a]). The crude product was purified by kugelrohr distillation (110–120°C/0.001 Torr) furnishing 4.10 g (90%) of **10b** as a colorless liquid. – IR: $\tilde{\nu}$ = 2180 (s, C≡C), 1720 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.30 (t, 3H, *J* = 7.1 Hz, CH_3), 1.61–1.66 (m, 4H, 4′-, 5′-H), 2.14–2.18 (m, 4H, 3′-, 6′-H), 4.21 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 6.16 (d, 1H, *J* = 15.8 Hz, 2-H), 6.25 (m, 1H, 2′-H), 6.89 (d, 1H, *J* = 15.8 Hz, 3-H). – ^{13}C NMR: δ = 14.3 (+, CH_3), 21.4 (−, C-5′), 22.2 (−, C-4′), 26.0 (−, C-3′), 28.9 (−, C-6′), 60.6 (−, CO_2CH_2), 84.2 (×, C-4/C-5), 100.7 (×, C-4/C-5), 120.5 (×, C-1′), 125.7 (+, C-2/C-3), 129.0 (+, C-2/C-3), 138.0 (+, C-2′), 166.2 (×, C-1). – MS: *m/z* (%) = 204 (63) [M^+], 91 (100).

$C_{13}H_{16}O_2$ (204.3) Calcd. C 76.44 H 7.90
Found C 76.76 H 7.78

10-Methyl-3,9-undecadien-5-yn-2-one (**10h**)[16b,19]: To a solution of 3.25 g (30 mmol) of a 9:1 mixture of 2-methyl-2-hepten-6-yne and 6-methyl-1,2,5-heptatriene[33] in 25 ml of diethyl ether *n*-BuLi (16.7 ml, 25 mmol, 1.5 M solution in hexane) was added dropwise at 0°C. The mixture was cooled to −30°C and 6.35 g (25 mmol) of iodine was added in one portion. The cooling bath was removed, and the mixture was allowed to warm up until the iodine was dissolved completely (ca. 0°C). After addition of 200 ml of water the organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ solution and dried with $MgSO_4$. The crude 7-iodo-2-methyl-2-heptcn-6-yne obtained after removal of the solvent in vacuo was used in the following reaction without further purification. – A suspension of 7.95 g (75 mmol) of Na_2CO_3, 9.36 g (30 mmol) of benzyltributylammonium chloride, and 10.5 g (150 mmol) of 3-buten-2-one in 5 ml of DMF was stirred at room temp. for 10 min. After addition of 0.2 g of $Pd(OAc)_2$ stirring was continued for another 5 min. A solution of the crude iodoalkyne in 20 ml of DMF was added dropwise (cooling with a water bath), and the mixture was stirred at room temp. for 16 h. Volatile components were removed under reduced pressure with a rotary evaporator, and the residue was diluted with 150 ml of diethyl ether. After filtration through a short silica gel column the filtrate was washed with water and dried with $MgSO_4$. The solvent was removed in vacuo and the crude product purified by column chromatography (silica gel 70–230 mesh, diethyl ether/hexane = 1:9); yield 1.75 g (40%) **10h** as a bright yellow liquid. – IR: = 2205 (s, C≡C),

1670 cm^{-1} (s, C=O). – ^1H NMR: δ = 1.61 (s, 3H, 10-CH_3), 1.69 (s, 3H, 11-H), 2.23 (s, 3H, 1-H), 2.24 (m, 2H, 7-H/8-H), 2.37 (m, 2H, 7-H/8-H), 5.14 (m, 1H, 9-H), 6.38 (d, 1H, *J* = 16.1 Hz, 3-H), 6.58 (dt, 1H, *J* = 16.1/2.2 Hz, 4-H). – ^{13}C NMR: δ = 17.7 (+, 10-CH_3), 20.4 (–, C-7), 25.6 (+, C-11), 27.0 (–, C-8), 27.3 (+, C-1), 78.3 (×, C-5/C-6), 80.3 (×, C-5/C-6), 122.3 (+, C-4), 124.8 (+, C-9), 133.4 (×, C-10), 137.5 (+, C-3), 197.1 (×, C-2). – MS: *m/z* (%) = 176 (3) [M^+], 59 (100).

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15
Found C 81.39 H 8.82

Ethyl 5-Phenyl-2-penten-4-ynethioate (**10i**)[20]: To a solution of 1.00 g (5.0 mmol) of **10a** in 15 ml of THF 0.73 g (5.5 mmol) of aluminium trichloride and 1.34 g (10.0 mmol) of (ethylthio)-trimethylsilane were added. The mixture was stirred at 40°C for 1 d. The reaction was quenched by pouring the mixture into stirred 0.1 M phosphate buffer solution (50 ml); the organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by kugelrohr distillation (140–150°C/0.001 Torr); yield 1.04 g of **10i** (96%, bright yellow liquid). – IR: ṽ = 2200 (s, C≡C), 1660 cm^{-1} (s, C=O). – ^1H NMR: δ = 1.29 (t, 3H, *J* = 7.4 Hz, CH_3), 2.96 (q, 2H, *J* = 7.4 Hz, CH_2), 6.55 (d, 1H, *J* = 15.6 Hz, 2-H), 6.90 (d, 1H, *J* = 15.6 Hz, 3-H), 7.34–7.37 (m, 3H, phenyl-H), 7.46–7.49 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 14.6 (+, CH_3), 23.5 (–, CH_2), 86.7 (×, C-4/C-5), 98.7 (×, C-4/C-5), 120.6 (+), 122.2 (×, phenyl), 128.5 (+), 129.4 (+), 132.0 (+), 136.0 (+, C-2/C-3/phenyl), 188.8 (×, C-1). – MS: *m/z* (%) = 216 (8) [M^+], 155 (100).

$C_{13}H_{12}OS$ (216.3) Calcd. C 72.19 H 5.59
Found C 71.78 H 5.80

General Procedure for the Preparation of Allenes by 1,6-Addition of Organocuprates to Polarized Enynes: To a suspension of 5.5 mmol of copper(I) iodide or cyanide in 20 ml of diethyl ether 11.0 mmol of the organolithium compound in diethyl ether (MeLi, PhLi), hexane (*n*-BuLi), or pentane (*t*-BuLi) is added dropwise. The temperature is kept at 0°C (MeLi) and –30°C (PhLi, *n*-BuLi, *t*-BuLi), respectively. The mixture is stirred for 30 min and a solution of 5.0 mmol of the enyne **10** in 20 ml of diethyl ether is added dropwise at –20°C; stirring at this temp. is continued for 1 h prior to workup.

Workup Procedure A: The mixture is poured into vigorously stirred 2 N H_2SO_4 (10 ml). The copper salts and excess of acid are removed by filtration through Celite. The filtrate is dried with $MgSO_4$ and the solvent removed in vacuo. The crude product is purified by kugelrohr distillation.

Workup Procedure B: The mixture is cooled to –80°C and added with a cannula to a stirred solution of 2.04 g (20 mmol) of pivalic acid in 20 ml of diethyl ether, which is kept at –80°C. After warming up to room temp., 10 ml of water is added, and the copper salts are removed by filtration through Celite. The filtrate is dried with $MgSO_4$ and the solvent removed in vacuo. The crude product is purified by kugelrohr distillation.

Ethyl 5-Phenyl-3,4-hexadienoate (**15a**): From 1.00 g (5.0 mmol) of **10a**, 1.05 g (5.5 mmol) of CuI, and 7.3 ml (11.0 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure A. Purification by kugelrohr distillation (110–120°C/0.001 Torr); yield 0.85 g of **15a** (79%, colorless liquid). – IR: ṽ = 1955 (w, C=C=C), 1730 cm^{-1} (s, C=O). – ^1H NMR: δ = 1.28 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 2.12 (d, 3H, *J* = 3.0 Hz, 6-H), 3.14 (d, 2H, *J* = 7.2 Hz, 2-H), 4.19 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 5.61 (tq, 1H, *J* = 7.2/3.0 Hz, 3-H), 7.22–7.25 (m, 1H, phenyl-H), 7.31–7.37 (m, 2H, phenyl-H), 7.42–7.45 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 14.2 (+, $CO_2CH_2CH_3$), 16.8 (+, C-6), 34.8 (–, C-2), 60.7 (–, CO_2CH_2), 86.2 (+, C-3), 101.7 (×, C-5), 125.8 (+), 126.8 (+), 128.3 (+), 136.8 (×, phenyl), 171.4 (×, C-1), 205.4 (×, C-4). – MS: *m/z* (%) = 216 (55) [M^+], 128 (100).

$C_{14}H_{16}O_2$ (216.3) Calcd. C 77.74 H 7.46
Found C 77.04 H 7.41

Ethyl 5-(1-Cyclohexen-1-yl)-3,4-hexadienoate (**15b**): From 1.02 g (5.0 mmol) of **10b**, 1.05 g (5.5 mmol) of CuI, and 7.3 ml (11.0 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure A. Purification by kugelrohr distillation (110–120°C/0.001 Torr); yield 0.90 g of **15b** (75%, colorless liquid). – IR: ṽ = 1950 (w, C=C=C), 1740 cm^{-1} (s, C=O). – ^1H NMR: δ = 1.26 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.56–1.65 (m, 4H, 4′-, 5′-H), 1.83 (d, 3H, *J* = 2.6 Hz, 6-H), 2.06–2.14 (m, 4H, 3′-, 6′-H), 3.01 (d, 2H, *J* = 7.1 Hz, 2-H), 4.15 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 5.37 (m, 1H, 3-H), 5.69 (m, 1H, 2′-H). – ^{13}C NMR: δ = 14.2 (+, $CO_2CH_2CH_3$), 16.1 (+, C-6), 22.4 (–, C-4′/C-5′), 22.9 (–, C-4′/C-5′), 26.0 (–, C-3′/C-6′), 26.9 (–, C-3′/C-6′), 35.4 (–, C-2), 60.6 (–, CO_2CH_2), 85.2 (+, C-3), 103.9 (×, C-5), 123.2 (+, C-2′), 133.3 (×, C-1′), 171.6 (×, C-1), 205.4 (×, C-4). – MS: *m/z* (%) = 220 (36) [M^+], 105 (100).

$C_{14}H_{20}O_2$ (220.3) Calcd. C 76.33 H 9.15
Found C 76.43 H 9.54

Ethyl 5-(Trimethylsilyl)-3,4-hexadienoate (**15c**): From 0.98 g (5.0 mmol) of **10c**[14], 1.05 g (5.5 mmol) of CuI, and 7.3 ml (11.0 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure A. Purification by kugelrohr distillation (70°C/0.3 Torr); yield 0.61 g of **15c** (57%, colorless liquid). – IR: ṽ = 1945 (w, C=C=C), 1735 cm^{-1} (s, C=O). – ^1H NMR: δ = 0.07 [s, 9H, $Si(CH_3)_3$], 1.25 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.67 (d, 3H, *J* = 2.9 Hz, 6-H), 2.94 (d, 2H, *J* = 7.2 Hz, 2-H), 4.13 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 4.86 (tq, 1H, *J* = 7.2/2.9 Hz, 3-H). – ^{13}C NMR: δ = –2.0 [+, $Si(CH_3)_3$], 14.2 (+, $CO_2CH_2CH_3$), 15.2 (+, C-6), 34.7 (–, C-2), 60.5 (–, CO_2CH_2), 77.5 (+, C-3), 92.4 (×, C-5), 172.0 (×, C-1), 206.0 (×, C-4). – MS: *m/z* (%) = 212 (6) [M^+], 73 (100).

$C_{11}H_{20}O_2Si$ (212.4) Calcd. C 62.21 H 9.49
Found C 64.89 H 9.07

Ethyl 5-Methyl-3,4-nonadienoate (**15d**): From 0.45 g (2.5 mmol) of **10d**[15], 0.51 g (2.7 mmol) of CuI, and 3.6 ml (5.4 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure B. Purification by kugelrohr distillation (70–80°C/0.001 Torr); yield 0.35 g of **15d** (71%, colorless liquid). – IR: ṽ = 1970 (w, C=C=C), 1735 cm^{-1} (s, C=O). – ^1H NMR: δ = 0.88 (t, 3H, *J* = 7.1 Hz, 9-H), 1.25 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.26–1.42 (m, 4H, 7-, 8-H), 1.66 (d, 3H, *J* = 2.8 Hz, 5-CH_3), 1.92 (m, 2H, 6-H), 2.95 (d, 2H, *J* = 7.1 Hz, 2-H), 4.13 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 5.12 (m, 1H, 3-H). – ^{13}C NMR: δ = 13.9 (+, C-9), 14.2 (+, $CO_2CH_2CH_3$), 16.9 (+, 5-CH_3), 22.3 (–, C-8), 29.5 (–, C-7), 33.5 (–, C-2/C-6), 35.5 (–, C-2/C-6), 60.5 (–, CO_2CH_2), 83.2 (+, C-3), 100.8 (–, C-5), 171.7 (×, C-1), 202.5 (×, C-4). – MS: *m/z* (%) = 196 (12) [M^+], 82 (100).

$C_{12}H_{20}O_2$ (196.3) Calcd. C 73.43 H 10.27
Found C 72.85 H 10.49

Ethyl 5-Phenyl-3,4-nonadienoate (**15e**): From 0.50 g (2.5 mmol) of **10a**, 0.27 g (3.0 mmol) of CuCN, and 4.0 ml (6.0 mmol) of *n*-BuLi (1.5 M solution in hexane); workup procedure B. Purification by kugelrohr distillation (150–160°C/0.001 Torr); yield 0.45 g of **15e** (70%, bright yellow liquid). – IR: ṽ = 1950 (w, C=C=C), 1735 cm^{-1} (s, C=O). – ^1H NMR: δ = 0.94 (t, 3H, *J* = 7.2 Hz, 9-H), 1.28 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.38–1.58 (m, 4H, 7-, 8-H), 2.45 (dt, 2H, *J* = 3.0/7.9 Hz, 6-H), 3.14 (d, 2H, *J* = 7.2 Hz, 2-H), 4.18 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 5.64 (tt, 1H, *J* = 7.2/3.0

Hz, 3-H), 7.19–7.24 (m, 1H, phenyl-H), 7.30–7.36 (m, 2H, phenyl-H), 7.41–7.46 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 14.0 (+, C-9), 14.2 (+, $CO_2CH_2CH_3$), 22.5 (–, C-8), 29.5 (–, C-6/C-7), 30.0 (–, C-6/C-7), 35.1 (–, C-2), 60.8 (–, CO_2CH_2), 87.4 (+, C-3), 107.1 (×, C-5), 126.1 (+), 126.8 (+), 128.2 (+), 136.7 (×, phenyl), 171.5 (×, C-1), 205.1 (×, C-4). – MS: *m/z* (%) = 258 (10) [M^+], 128 (100).

$C_{17}H_{22}O_2$ (258.4) Calcd. C 79.03 H 8.58
Found C 78.76 H 8.70

Ethyl 6,6-Dimethyl-5-phenyl-3,4-heptadienoate (**15f**): From 0.50 g (2.5 mmol) of **10a**, 0.36 g (4.0 mmol) of CuCN, and 4.7 ml (8.0 mmol) of *t*-BuLi (1.7 M solution in pentane); workup procedure A. Purification by kugelrohr distillation (120–130°C/0.001 Torr); yield 0.52 g of **15f** (81%, colorless liquid). – IR: ṽ = 1960 (w, C=C=C), 1730 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.15 [s, 9H, $C(CH_3)_3$], 1.25 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 3.05 (d, 2H, *J* = 7.1 Hz, 2-H), 4.12 (q, 2H, *J* = 7.1 Hz, CO_2CH_2), 5.35 (t, 1H, *J* = 7.1 Hz, 3-H), 7.22–7.32 (m, 5H, phenyl-H). – ^{13}C NMR: δ = 14.1 (+, $CO_2CH_2CH_3$), 29.8 [+, $C(CH_3)_3$], 34.2 [×, $C(CH_3)_3$], 35.4 (–, C-2), 60.6 (–, CO_2CH_2), 84.7 (+, C-3), 117.0 (×, C-5), 126.7 (+), 127.7 (+), 129.3 (+), 137.5 (×, phenyl), 171.4 (×, C-1), 202.8 (×, C-4). – MS: *m/z* (%) = 258 (37) [M^+], 57 (100).

$C_{17}H_{22}O_2$ (258.4) Calcd. C 79.03 H 8.58
Found C 78.70 H 8.73

Ethyl 3-Methyl-5-phenyl-3,4-hexadienoate (**15g**): From 0.54 g (2.5 mmol) of **10e**[17], 0.51 g (2.7 mmol) of CuI, and 3.6 ml (5.4 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure B. Purification by kugelrohr distillation (120–130°C/0.001 Torr); yield 0.43 g of **15g** (75%, colorless liquid). – IR: ṽ = 1955 (w, C=C=C), 1730 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.25 (t, 3H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.87 (s, 3H, 3-CH_3), 2.09 (s, 3H, 6-H), 3.09/3.10 (2 × s, 2H, 2-H), 4.15/4.15 (2 × q, 2H, 2 × *J* = 7.1 Hz, CO_2CH_2), 7.18–7.45 (m, 5H, phenyl-H). – ^{13}C NMR: δ = 14.2 (+, $CO_2CH_2CH_3$), 17.0 (+, 3-CH_3/C-6), 18.9 (+, 3-CH_3/C-6), 40.4 (–, C-2), 60.7 (–, CO_2CH_2), 94.3 (×, C-3/C-5), 100.2 (×, C-3/C-5), 125.9 (+), 126.5 (+), 128.2 (+), 137.6 (×, phenyl), 171.3 (×, C-1), 203.2 (×, C-4). – MS: *m/z* (%) = 230 (57) [M^+], 141 (100).

$C_{15}H_{18}O_2$ (230.3) Calcd. C 78.23 H 7.88
Found C 76.70 H 7.73

Ethyl 2-Methyl-5-phenyl-3,4-hexadienoate (**15h**): From 0.54 g (2.5 mmol) of **10f**[18], 0.51 g (2.7 mmol) of CuI, and 3.6 ml (5.4 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure B. Purification by kugelrohr distillation (120–130°C/0.001 Torr); yield 0.36 g of **15h** (62%, colorless liquid) as a 1:1 mixture of diastereomers. – IR: ṽ = 1950 (w, C=C=C), 1730 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.25/1.26 (2 × t, 3H, 2 × *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.30/1.32 (2 × d, 3H, 2 × *J* = 2.3 Hz, 2-CH_3), 2.10/2.11 (2 × d, 3H, 2 × *J* = 2.9 Hz, 6-H), 3.24 (m, 1H, 2-H), 4.15/4.16 (2 × q, 2H, 2 × *J* = 7.1 Hz, CO_2CH_2), 5.63 (dq, 1H, *J* = 2.9/6.4 Hz, 3-H), 7.17–7.43 (m, 5H, phenyl-H). – ^{13}C NMR: δ = 14.1 (+, $CO_2CH_2CH_3$), 16.49/16.54 (+, 2-CH_3/C-6), 16.87/16.93 (+, 2-CH_3/C-6), 39.73/39.78 (+, C-2), 60.7 (–, CO_2CH_2), 93.5 (+, C-3), 102.86/103.05 (×, C-5), 125.7 (+), 126.7 (+), 128.3 (+), 136.7 (×, phenyl), 174.3 (×, C-1), 203.9 (×, C-4). – MS: *m/z* (%) = 230 (16) [M^+], 77 (100).

$C_{15}H_{18}O_2$ (230.3) Calcd. C 78.23 H 7.88
Found C 78.25 H 8.01

7,7-Dimethyl-6-phenyl-4,5-octadien-2-one (**15i**): From 0.43 g (2.5 mmol) of **10g**[19], 0.36 g (4.0 mmol) of CuCN, and 4.7 ml (8.0 mmol) of *t*-BuLi (1.7 M solution in pentane); workup with 0.1 N H_2SO_4 (100 ml) at 0°C according to procedure A. Purification by kugelrohr distillation (110–120°C/0.001 Torr); yield 0.37 g of **15i** (65%, colorless liquid). – IR: ṽ = 1955 (w, C=C=C), 1715 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.15 [s, 9H, $C(CH_3)_3$], 2.14 (s, 3H, 1-H), 3.13 (d, 2H, *J* = 7.2 Hz, 3-H), 5.36 (t, 1H, *J* = 7.2 Hz, 4-H), 7.23–7.34 (m, 5H, phenyl-H). – ^{13}C NMR: δ = 29.3 (+, C-1), 29.8 [+, $C(CH_3)_3$], 34.3 [×, $C(CH_3)_3$], 44.3 (–, C-3), 84.4 (+, C-4), 116.6 (×, C-6), 126.6 (+), 127.7 (+), 129.2 (+), 137.3 (×, phenyl), 202.6 (×, C-2/C-5), 206.2 (×, C-2/C-5). – MS: *m/z* (%) = 228 (13) [M^+], 43 (100).

$C_{16}H_{20}O$ (228.3) Calcd. C 84.16 H 8.83
Found C 83.69 H 8.81

Ethyl 5-Phenyl-3,4-hexadienethioate (**15j**): From 0.54 g (2.5 mmol) of **10i**, 0.51 g (2.7 mmol) of CuI, and 3.6 ml (5.4 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure B. Purification by kugelrohr distillation (140–150°C/0.001 Torr); yield 0.38 g of **15j** (65%, colorless liquid). – IR: ṽ = 1950 (w, C=C=C), 1680 cm^{-1} (s, C=O). – ^{1}H NMR: δ = 1.26 (t, 3H, *J* = 7.4 Hz, $COSCH_2CH_3$), 2.11 (d, 3H, *J* = 2.9 Hz, 6-H), 2.90 (q, 2H, *J* = 7.4 Hz, $COSCH_2$), 3.31 (d, 2H, *J* = 7.5 Hz, 2-H), 5.57 (tq, 1H, *J* = 7.5/2.9 Hz, 3-H), 7.18–7.44 (m, 5H, phenyl-H). – ^{13}C NMR: δ = 14.7 (+, $COSCH_2CH_3$), 16.8 (+, C-6), 23.5 (–, $COSCH_2$), 44.0 (–, C-2), 86.0 (+, C-3), 101.9 (×, C-5), 125.9 (+), 126.7 (+), 128.3 (+), 136.5 (×, phenyl), 197.4 (×, C-1), 206.2 (×, C-4). – MS: *m/z* (%) = 232 (7) [M^+], 128 (100).

$C_{14}H_{16}OS$ (232.4) Calcd. C 72.36 H 6.94
Found C 72.30 H 7.37

6,10-Dimethyl-3,5,9-undecatrien-2-one (**18**): From 0.44 g (2.5 mmol) of **10h**, 0.51 g (2.7 mmol) of CuI, and 3.6 ml (5.4 mmol) of MeLi (1.5 M solution in diethyl ether); workup procedure A. The crude product consisted of allene **17** and diene **18** in a ratio of 1:2 (^{1}H-NMR analysis). The mixture was treated with methanolic NaOH according to ref.[27]. Purification by kugelrohr distillation (90–100°C/0.001 Torr) furnished 0.23 g of **18** (48%, bright yellow liquid) as a mixture of 3,5-*E*/*Z* isomers.

CAS-Registry-Numbers

10a: 117552-48-4 / **10b**: 127915-51-9 / **10c**: 54599-61-0 / **10d**: 64576-91-6 / **10e**: 92495-95-9 / **10f**: 54355-86-1 / **10g**: 63923-00-2 / **10h**: 127915-52-0 / **10i**: 127915-53-1 / **12a**: 2579-22-8 / **12b**: 15341-64-7 / **13**: 867-13-0 / **15a**: 127915-54-2 / **15b**: 127915-55-3 / **15c**: 127915-56-4 / **15d**: 127915-57-5 / **15e**: 127915-58-6 / **15f**: 127915-59-7 / **15g**: 127915-60-0 / **15h** (isomer 1): 127915-61-1 / **15h** (isomer 2): 127915-65-5 / **15i**: 127915-62-2 / **15j**: 127915-63-3 / **18**: 141-10-6 / Me_2CuLi: 15681-48-8 / *n*-Bu_2CuLi: 24406-16-4 / *n*-BuCu(C≡CBu)Li: 62197-73-3 / *n*-$Bu_2Cu(CN)Li$: 80473-69-4 / *n*-BuCu(CN)Li: 41742-63-6 / *n*-BuCu · BF_3: 65139-99-3 / Ph_2CuLi: 23402-69-9 / *t*-$Bu_2Cu(CN)Li_2$: 87263-84-1 / 2-methyl-2-hepten-6-yne: 22842-10-0 / 3-buten-2-one: 78-94-4 / 7-iodo-2-methyl-2-hepten-6-yne: 127915-64-4

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