Allenyl Enolates — A New Class of Chiral Ambident Nucleophiles, 1

Reaction with C and Si Electrophiles

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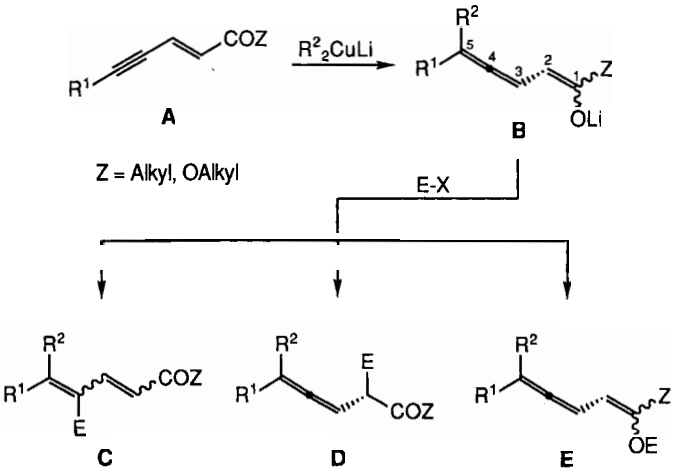
The regio- and stereoselectivity of the reaction of allenyl enolates obtained by 1,6-addition of lithium dimethylcuprate to acceptor-substituted enynes **1** with C and Si electrophiles is examined. It is found that allyl bromide reacts at C-4 to give 4-substituted 2,4-dienoates **2**; in contrast, methyl triflate and carbonyl compounds react at C-2 to yield 2-substituted β-allenic esters **3**–**12**. The hard electrophile chlorotrimethylsilane reacts at the enolate oxygen atom to provide allenyl enol ether **14**. The regioselectivity of these trapping reactions depends only on the nature of the electrophile; the stereoselectivities, on the other hand, are a function of both the steric properties of the allenyl enolate and the type of electrophile. The regio- and stereoselectivities are rationalized in terms of charge control and frontier-orbital control, of kinetic and thermodynamic control, and of steric interactions in intermediates and transition states.

The formation of C–C bonds by the reaction of enolates with electrophiles is an important synthetic method in organic chemistry, in particular because a high degree of stereocontrol may be achieved in these processes[1]. This transformation can be carried out in a classical manner via deprotonation of carbonyl compounds[1]; synthetically more useful, however, is the reaction of enolates formed by 1,4-addition of nucleophiles to Michael acceptors with electrophiles since two different substituents can be introduced in one sequence[2]. Likewise, deprotonation of α,β-unsaturated carbonyl compounds gives rise to the formation of dienolates; these ambident nucleophiles can react with electrophiles at the α- or the γ-position[1e,3]. Usually, reaction at the α-position predominates; however, in many cases mixtures of the two regioisomers are formed[1e,3], a fact that limits the synthetic use of this method. In this paper we disclose our results of the reaction of allenyl enolates, which represent a new class of chiral ambident nucleophiles, with different electrophiles[4]. Allenyl enolates are readily available by 1,6-addition of organocuprates to acceptor-substituted enynes[4,5] and can react with an electrophile at C-4, at C-2, or at the enolate oxygen atom; in contrast to the dienolates mentioned above, a complete regiocontrol can be achieved in these reactions[6].

According to their NMR spectra, the allenyl enolates formed by 1,6-addition of organocuprates to acceptor-substituted enynes **A** are represented best by structure **B** with the lithium atom bound to the enolate oxygen[7,8]; alternative species with the lithium at C-2 or C-4 (possibly π-bound[9]) could not be detected. Nevertheless, all three possible regioisomeric products resulting from attack of an electrophile *E*–*X* at C-4 (**C**), C-2 (**D**), and the enolate oxygen atom (**E**) can be obtained. The regioselectivity of the reaction has consequences for the stereochemical outcome: if the attack



occurs at C-4 or at the enolate oxygen, (*E*/*Z*) isomers can be formed; if the reaction takes place at C-2, the product **D** possesses two stereogenic elements and therefore exists as pair of diastereomers. The goal of this study is to establish whether the regio- and stereochemical course of the reaction of allenyl enolates with electrophiles can be controlled by the type of electrophile, by the steric and electronic properties of the starting enyne **A**, and by the reaction conditions.

Results

For the reaction of allenyl enolates with soft carbon electrophiles, three 2-en-4-ynoates **1a**–**c** with different steric properties were used; for the reaction with chlorotrimethylsilane, ketone **1d** was employed. All enynes are readily available by standard methods[10].

For the first trapping reactions of allenyl enolates alkylating agents were used. Whereas the enolate obtained by 1,6-addition of lithium dimethylcuprate ($Me_2CuLi \cdot LiI$) to

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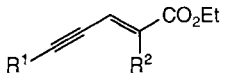
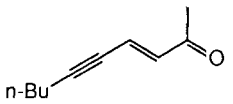


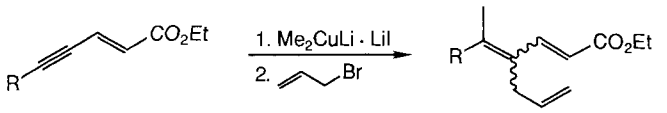
1a: R^1 = n-Bu, R^2 = H

1b: R^1 = t-Bu, R^2 = H

1c: R^1 = n-Bu, R^2 = Me



1d



1a: R = n-Bu

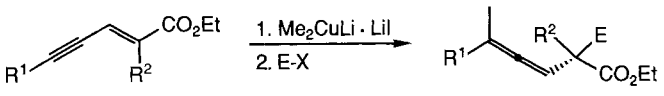
1b: R = t-Bu

2a (60%, E : Z = 1 : 1)

2b (80%, E : Z = >99 : <1)

1a does not react with methyl iodide and benzyl bromide, a rapid reaction takes place with allyl bromide at −20 °C, proceeding with exclusive attack of the electrophile at C-4 of the allenyl enolate to give the 4-allyl-substituted 2,4-dienoate **2a** in 60% yield. Likewise, the *tert*-butyl-substituted enynoate **1b** furnished dienoate **2b** in 80% yield under the same conditions; thus, the regioselectivity of the attack of allyl bromide is not altered by the presence of the bulky *tert*-butyl group at C-5. Theses transformations take place not only regioselectively but also with remarkable stereoselectivity: whereas **2a** is formed as a 1:1 mixture of the (2*E*,4*E*) and (2*E*,4*Z*) isomers, **2b** is obtained as (2*E*,4*E*) isomers exclusively (proven with NOE difference spectra; see Experimental Section). The geometry of the C-2/C-3 double bond seems to be thermodynamically controlled; in contrast to this, the stereochemistry of the attack of the electrophile at the allenyl enolate and consequently the geometry of the C-4/C-5 double bond should be influenced by the size of the substituents at C-5. If these substitutents differ considerably in size, one might expect a preference of the attack from the side of the smaller substituent; such a behavior is found for example in the base-catalyzed isomerizations of β-allenic carbonyl compounds to conjugated dienes[11,12]. Thus, the formation of a 1:1 mixture of (*E*/*Z*) isomers for **2a** may be rationalized by the small difference in size between the methyl and *n*-butyl group. However, in the case of **2b** the product resulting from attack of the electrophile from the sterically more shielded side of the allenyl enolate, i.e. the side occupied by the *tert*-butyl group, is formed exclusively! The stereoselectivity of this reaction is affected slightly by addition of the lithium-complexing agent 12-crown-4 to the enolate formed from **1b** and $Me_2CuLi \cdot LiI$; treatment with allyl bromide then yields **2b** as a 5:1 mixture of the (2*E*,4*E*) and (2*E*,4*Z*) isomers, i.e. under these conditions a small shift towards the product expected on sterical grounds is observed. Possible explanations for this puzzling behavior will be discussed below.

Like allyl bromide, propargyl bromide reacts with the allenyl enolate obtained by 1,6-addition of $Me_2CuLi \cdot LiI$ to **1a** at C-4 exclusively. However, the synthetic use of this reaction is limited by the fact that it takes place both in an



1a - c **3 - 12**

Table 1. Reaction of 2-en-4-ynoates **1** with $Me_2CuLi \cdot LiI$ and electrophiles E−X

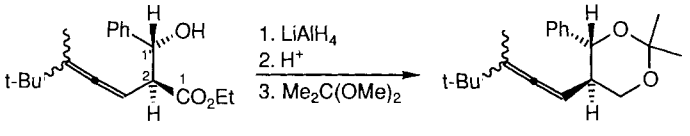
Entry	Enyne	Electrophile	Allene	R^1	R^2	E	Yield	dr
1	**1a**	MeOTf	**3**	n-Bu	H	Me	71%	1:1
2	**1b**	MeOTf	**4**	t-Bu	H	Me	51%	1:1
3	**1c**	MeOTf	**5**	n-Bu	Me	Me	80%	-
4	**1a**	PhCHO	**6**	n-Bu	H	CHPhOH	79%	~1:1:1:1
5	**1b**	PhCHO	**7**	t-Bu	H	CHPhOH	99%	8:8:4:1
6	**1c**	PhCHO	**8**	n-Bu	Me	CHPhOH	62%	1:1:1:1
7	**1b**	t-BuCHO	**9**	t-Bu	H	CH(t-Bu)OH	82%	1:1
8	**1a**	CH_2=CHCHO	**10**	n-Bu	H	CH(CH=CH_2)OH	53%	~1:1:1:1
9	**1a**	MeCOMe	**11**	n-Bu	H	CMe_2OH	71%	1:1
10	**1b**	MeCOMe	**12**	t-Bu	H	CMe_2OH	83%	4:1

S_N2 and S_N2' fashion, furnishing a mixture of 4-propargyl- and 4-allenyl-substitued 2,4-dienoates[4b].

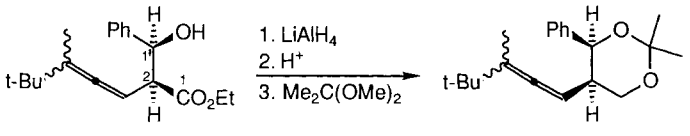
Since to our surprise the allenyl enolates did not react with methyl iodide, we next tried to use the more reactive methyl triflate for this purpose. Indeed, the allenyl enolate formed from **1a** and $Me_2CuLi \cdot LiI$ reacts with methyl triflate; however, the only product obtained in 71% yield was the methylated allene **3** (see Table 1, entry 1), i.e. the reaction takes place at C-2 exclusively! Likewise, the enynoates **1b** and **1c** furnished allenes **4** and **5** in 51 and 80% yield, respectively (entries 2 and 3). Thus, this method allows to synthesize β-allenic esters with a quarternary center at C-2; besides that, the formation of **5** proves that the regioselectivity of this trapping reaction is insensitive towards the steric properies of the allenyl enolate. The products **3** and **4** were obtained as 1:1 mixtures of diastereomers, i.e. the reaction proceeds without diastereoselectivity.

Carbonyl compounds turned out to be reactive towards allenyl enolates obtained by 1,6-addition of organocuprates to 2-en-4-ynoates **1** − **c**, too. Thus, treatment of **1a** with $Me_2CuLi \cdot LiI$ and benzaldehyde at −20 °C afforded in 79% yield the β-hydroxy ester **6** resulting from exclusive attack of the aldehyde at C-2 of the enolate (Table 1, entry 4). Similarly, substrates **1b** and **1c** gave the adducts **7** and **8** in 99 and 62% yield, respectively (entries 5 and 6). The products **6**−**8** possess three stereogenic elements and thus exist as four diastereomers. In these cases all four diastereomers were obtained, although with different diastereoselectivities: whereas for the *n*-butyl-substituted products **6** and **8** almost equal amounts of the four diastereomers were produced, the *tert*-butyl-substituted adduct **7** was isolated as a 8:8:4:1 mixture of diastereomers.

This mixture could be separated partially by column chromatography into two fractions consisting of the two major and the two minor diastereomers, respectively. In order to assign the relative configuration, the mixture of the two major diastereomers (**7a/b**) was converted into the cyclic ketals **13a/b** by reduction of the ester function with $LiAlH_4$ and ketalization with 2,2-dimethoxypropane. The relative con-



7a/b **13a/b**



7c/d **13c/d**

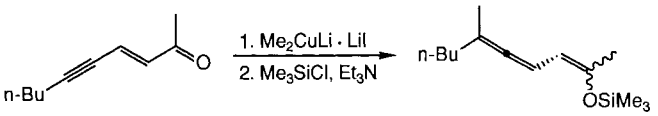
figuration of the two centers of chirality of the dioxane ring was assigned by determining the ^{1}H-NMR coupling constants of the two hydrogen atoms attached to these centers; values of J = 10.4/10.5 Hz were obtained for **13a/b**. Thus, the hydrogen atoms are *trans*[13], and the diastereomers **7a/b** possess the (1′*RS*,2*SR*) configuration and differ only in the relative configuration of the allene moiety. Analogous treatment of the minor isomers **7c/d** gave the ketals **13c/d**; here, a coupling constant of J = 2.1 Hz was determined for both diastereomeric ketals, proving a *cis*-configuration[13] for **13c/d** and a (1′*SR*,2*SR*) configuration for **7c/d**.

The formation of **7** is the first example of a trapping reaction of an allenyl enolate proceeding with (modest) diastereoselectivity. Encouraged by this result, we tried to improve the steroselectivity by using the bulkier pivalic aldehyde for trapping the allenyl enolate obtained from **1b** and $Me_2CuLi \cdot LiI$; indeed, the adduct **9** isolated in 82% yield consists of a 1:1 mixture of only two of the four possible diastereomers (entry 7). The relative configuration was assigned as for **7**; the mixture of diastereomeric ketals obtained from **9** gave coupling constants of J = 9.4/9.5 Hz, proving a *trans*-configuration of the dioxane ring[13] and a (1′*RS*,2*SR*) configuration for **9**. Thus, the diastereomers of **9** possess the same relative configuration as the two major diastereomers of **7**; in the trapping reaction with pivalic aldehyde the two minor diastereomers of type **7c/d** are no longer formed.

Another interesting aldehyde for trapping of the allenyl enolates is acrolein; here, the enolate could add in a 1,2- or in a 1,4-fashion to the enal moiety. Reaction of the allenyl enolate obtained from **1a** and $Me_2CuLi \cdot LiI$ with acrolein at −20°C gave adduct **10** (entry 8, 53% yield, 1:1:1:1 mixture of diastereomers); thus, in analogy to the reaction of other lithium enolates[1], the allenyl enolate reacts with acrolein with exclusive 1,2-addition.

The allenyl enolates obtained by treatment of enynoates **1a** and **1b** with $Me_2CuLi \cdot LiI$ reacted also with acetone at −20°C (Table 1, entries 9 and 10) to give the adducts **11** and **12** resulting from exclusive attack of the electrophile at C-2 of the enolates. These products possess two stereogenic elements and therefore exist as pair of diastereomers; whereas the *n*-butyl-substituted enynoate **1a** gave a 1:1 mixture of the two diastereomers, for the *tert*-butyl-substituted ester **1b** a larger degree of diastereoselection (4:1) was observed.

We also tried to use acetyl chloride for trapping allenyl enolates obtained by the 1,6-addition method. However, besides the β-keto esters resulting from attack of acetyl chloride at C-2 of the enolates, large amounts of β-hydroxy esters of type **11/12** were formed. The reason for this behavior is probably that acetyl chloride reacts reacts more rapidly with excess lithium dimethylcuprate present in the mixture than it is trapping the allenyl enolate; the acetone thus produced then reacts with the allenyl enolate to provide the products of type **11/12**. Although it should be possible to circumvent this problem by avoiding the presence of excess cuprate, we did not undertake further investigations in this direction since our main goal was to establish that acetyl chloride, like acetone and aldehydes, reacts with allenyl enolates regioselectively at C-2. In contrast to these carbonyl compounds, styrene oxide is not sufficiently reactive to trap the enolate obtained from **1a** and $Me_2CuLi \cdot LiI$[4b].



1d **14** (76%, E : Z = 1 : 2)

Finally, we tested the reaction of hard electrophiles like chlorotrimethylsilane with the allenyl enolate formed from ketone **1d** by 1,6-addition of lithium dimethylcuprate in order to obtain adducts of type **E** resulting from attack of the electrophile at the enolate oxygen atom (enynes with the ester function as acceptor substituent were not used for this purpose because additives like HMPTA are needed for the formation of ketene acetals and because these products are rather sensitive[2,14]). Indeed, treatment of this enolate with Me_3SiCl/Et_3N gave the allenyl enol ether **14** in 75% yield with an (*E*/*Z*) ratio of 1:2; the NMR signals for the isomers were assigned by using NOE difference spectra (see Experimental Section). The enol ether **14** is quite sensitive and decomposes already at room temperature; even more unstable, however, is the analogous enol triflate obtained by reaction of the allenyl enolate with *N*-phenylbis(trifluoromethanesulfonimide)[4b,15]. The regioselectivity of the trapping of the allenyl enolate obtained from 2-en-4-ynone **1d** and $Me_2CuLi \cdot LiI$ a with other electrophiles is analogous to that of the enolates derived from esters **1a**–**c**, i.e. allyl bromide reacts at C-4 and carbonyl compounds at C-2; the products thus formed, however, are rather unstable und could not be obtained in pure form[4b].

Allenyl enolates did not react with other heteroatom electrophiles; treatment of the enolate obtained from **1a** and $Me_2CuLi \cdot LiI$ with *N*-bromosuccinimide, *N*-chlorosuccinimide, and dimethyl disulfide, respectively, gave after aqueous workup only the protonated products ethyl 5-methyl-3,4-nonadienoate and ethyl 5-methyl-2,4-nonadienoate[4b]. The results of the reaction of allenyl enolates with iodine and oxidizing agents are presented in the following paper[16].

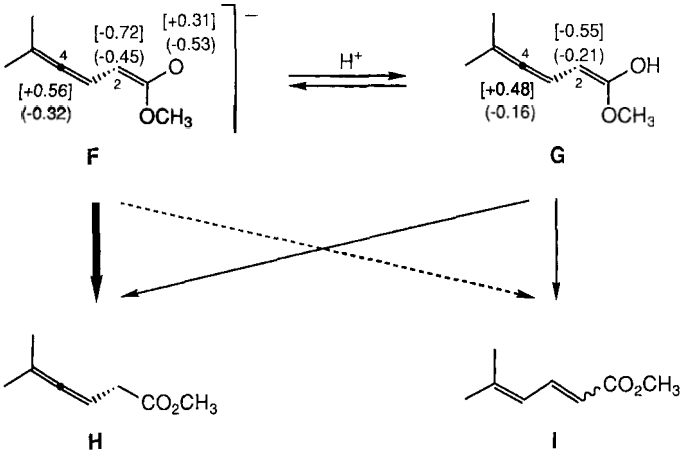
Discussion

The reactions of allenyl enolates with electrophiles presented in this paper provided several interesting and some-

times surprising results with regard to regioselectivity, (*E*/*Z*) selectivity, and diastereoselectivity. In this section, brief mechanistic considerations concerning these selectivity problems are made.

Regioselectivity

The regioselectivity of the reaction of allenyl enolates with electrophiles can be rationalized in terms of charge-controlled and frontier orbital-controlled interactions, respectively, between the reactants[17]; here, semiempirical MNDO calculations[18] proved to be a valuable tool. We have found earlier that the regioselectivity of the simplest trapping reaction of ester allenyl enolates, the protonation, can be controlled by the nature of the proton source; with the weak and bulky pivalic acid protonation takes place at C-2 exclusively to give β-allenic esters[4a]. Here, the equilibrium between the allenyl enolate **F** and the enol **G** has to be taken into account[19].



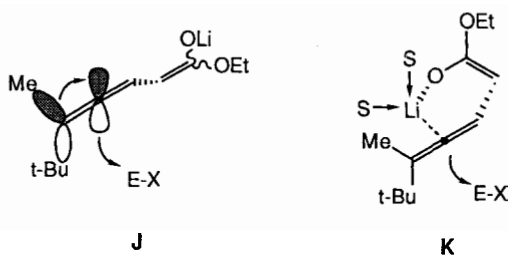
[...]: HOMO coefficients (MNDO) (...): Charge densities (MNDO)

If the protonation is carried out with a strong acid, the concentration of solvated protons is high; these are very hard electrophiles and react with charge control[17] at the enolate oxygen atom of enolate **F** (highest negative charge density: −0.53), shifting the equilibrium to the side of allenyl enol **G**. For the enol the charge densities (−0.21 vs. −0.16) as well as the HOMO coefficients (−0.55 vs. +0.48) at C-2 and C-4 are virtually identical; therefore, *C*-protonation with subsequent *O*-deprotonation should yield mixtures of allene **H** and conjugated diene **I**, regardless whether Coulomb or orbital interactions are more important. If, instead, the protonation is carried out with a weak acid, the concentration of solvated protons is low, and the products are formed via enolate **F**. The kinetically controlled protonation of **F** with a weak acid, which is acting as a soft electrophile, should be controlled by frontier orbital interactions[17]. The HOMO coefficient at C-2 (−0.72) is considerably larger than at C-4 (+0.56); therefore, allene **H** should be formed mainly. It is noteworthy that the protonation of keto allenyl enolates yields mainly[4a] or exclusively[5b] conjugated 2,4-dienones; here, thermodynamic control seems to dominate, favoring the formation of conjugated dienes of type **I** (according to our MNDO calculations, methyl (*E*)-2,4-pentadienoate is more stable than methyl 3,4-pentadienoate by 11.6 kcal/mol). Besides these electronic factores, steric influences also affect the regioselectivity of the protonation of allenyl enolates. The presence of bulky substitutents at C-5 of the enolate disfavors protonation at C-4 und therefore favors the formation of the allene **H**, in particular, if the proton source is also sterically demanding[4a,5a].

The factors controlling the regioselectivity of the protonation should also govern the reaction of allenyl enolates with other electrophiles: hard electrophiles should react with charge control at the enolate oxygen atom and soft electrophiles with frontier orbital control at C-2. This is in agreement with the experiment, e.g. with chlorotrimethylsilane and carbonyl compounds as electrophiles; in the latter case, interaction of the carbonyl oxygen atom of the electrophile with the lithium atom of the allenyl enolate favors reaction at C-2 even more[20]. An exemption is allyl bromide which attacks the allenyl enolate regioselectively at C-4; this reaction could proceed via a "late" product-like transition state and therefore could be controlled by the thermodynamic stability of the 2,4-dienoate formed. Alternatively, the attack of allyl bromide could take place first at C-2, providing 2-allyl-substituted β-allenic ester; subsequent Cope rearrangement could then lead to the observed products **2**. However, this possibility can be ruled out because 1,2,6-trienes analogous to these hypothetical intermediates are stable under the conditions employed for the preparation of **2a/b** and do not undergo Cope rearrangements[21].

(E/Z) Selectivity

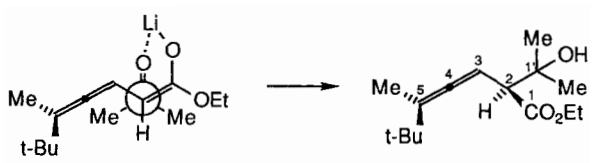
The (*E*/*Z*) selectivity observed in the formation of adduct **2b** from enynoate **1b** by treatment with lithium dimethylcuprate and allyl bromide is opposite to that expected from the steric influence of the substituents at C-5 of the allenyl enolate which should favor the (2*E*,4*Z*) product. One possible explanation for this behavior is the Cieplak effect, which has been used to account for unexpected stereochemical results of several reactions[22]. This bases on the assumption that the attack of the electrophile is controlled by delocalization of antiperiplanar σ bonds into the σ* orbital formed during the reaction[22]. Due to hyperconjugation, the σ bond to the methyl group is somewhat more electron-rich than that to the *tert*-butyl group[23]; therefore, the attack of the electrophile should be directed *anti* to the methyl group (see structure **J**).



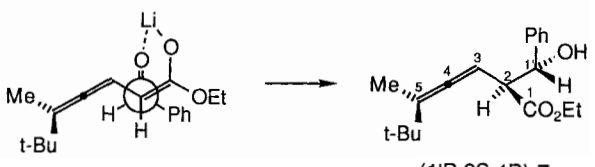
This effect, however, cannot account for the influence of the lithium-complexing agent 12-crown-4 on the (*E*/*Z*) selectivity. Rather, it seems reasonable to assume that the trapping reaction leading to **2b** is proceeding via a species of type **K** where the enolate lithium atom is coordinated to a π orbital of C-4 or to the C-3/C-4 π bond; although such a species could not be detected in the NMR spectra of allenyl enolates[7], it could be present as a minor species and, if sufficiently reactive, be on the reaction coordinate leading to product **2b**. The enolate lithium is rather bulky because it is coordinated to solvent molecules and/or copper species which are formed in the 1,6-addition reaction; therefore, the π interaction should take place preferably on the side of the allenyl enolate occupied by the smaller methyl group. Thus, the side of the *tert*-butyl group would be sterically less hindered and attack of allyl bromide from this side would give the observed (2*E*,4*E*) isomer. The presence of 12-crown-4 could cause a weakening of the π interaction; this would make the side of the allenyl enolate occupied by the methyl group accessible for the electrophile, and some (2*E*,4*Z*) product would be formed.

Diastereoselectivity

The reaction of allenyl enolates with methyl triflate and carbonyl compounds at C-2 proceeds in most cases without diastereoselectivity (products **3**, **4**, **6**, **8**, **10**, and **11**); however, in a few cases modest degrees of diastereoselectivity are observed, depending both on the electrophile (**7** vs. **9**) and on the structure of the allenyl enolate (**11** vs. **12**). There is ample precedent for aldol reactions of chiral ester enolates[24]; however, so far enolates with a center of chirality rather than a chirality axis have been used. In order to explain the observed stereoselectivites, the diastereomeric transition states leading to the different diastereomeric products have to be considered. For the reaction of the allenyl enolate derived from **1b** and $Me_2CuLi \cdot LiI$ with acetone the diastereoselectivity is independent on the geometry of the allenyl enolate; the transition state for the (*E*)-enolate with the smallest steric interactions is represented by structure **L**. Of the two diastereotopic sides of the allenyl enolate, the reaction should take place preferably on the side occupied by the smaller methyl group at C-5; therefore, (2*S*,4*R*)-**12** should be the main product. We are currently trying to verify this prediction experimentally. In the analogous reaction of the enynoate **1a**, the reaction can take place on the side of the methyl group or of the *n*-butyl group at C-5; since the difference in size between these groups is small, a 1:1 mixture of the two diastereomeric products is formed.



L (2S,4R)-**12**



M (1'R,2S,4R)-**7**

The situation changes if the allenyl enolate is trapped with aldehydes; now four diastereomers can be formed, and the stereochemical course depends on the geometry of the allenyl enolate[24]. The energetically most favorable transition state for the reaction of the (*E*)-allenyl enolate derived from **1b** and $Me_2CuLi \cdot LiI$ with benzaldehyde has structure **M**; again, the reaction should take place preferably on the side of the allenyl enolate occupied by the smaller methyl substituent at C-5. Of the two enantiotopic sides of the aldehyde, the reaction should proceed mainly on the *Re*-side, so that the aldehyde hydrogen points towards the groups at C-5 and the phenyl group to the sterically less hindered side of the enolate; thus, (1'*R*,2*S*,4*R*)-**7** should be the main product. This is in accordance with the experiment: for benzaldehyde the two diastereomers with the (1'*RS*,2*SR*) configuration are the major, for pivalic aldehyde the only products. The (*Z*)-allenyl enolate would give the opposite diastereoselectivities which are not consistent with the experiment; thus, the reaction seems to proceed mainly or exclusively via the (*E*)-enolate. In this context it is interesting to note that in the NMR spectrum of the allenyl enolate obtained by 1,6-addition of lithium di-*tert*-butylcyanocuprate to **1b** only one isomeric form could be detected; however, it could not yet be determined whether this has the (*E*) or (*Z*) geometry. Therefore, we will devote further work in order to determine whether the diastereoselectivity of the trapping reaction of allenyl enolates with carbonyl compounds is actually a function of the enolate geometry and whether factors like the presence of copper in the reaction mixture (which could form copper-containing clusters with the enolate and therefore influence the stereoselectivity) and the reaction conditions (the aldol reaction is reversible and can therefore take place under kinetic or thermodynamic control, usually with different stereoselectivites[24]) are affecting the stereochemical course of these trapping reactions.

Conclusions

In this work we have shown that the reaction of allenyl enolates obtained by 1,6-addition of lithium dimethylcuprate to acceptor-substituted enynes **1** with several electrophiles proceed with complete regioselectivity either at C-4, at C-2, or at the enolate oxygen atom of the allenyl enolate. Whereas allyl bromide reacts at C-4 to give 4-substituted 2,4-dienoates, methyl triflate and carbonyl compounds react at C-2 to yield 2-substituted β-allenic esters. The hard electrophile chlorotrimethylsilane is found to react at the enolate oxygen atom. The regioselectivity observed in these reactions does not depend on the steric and electonic properties of the starting enyne and on the reaction conditions but only on the nature of the electrophile. In contrast, the stereoselectivities of the trapping reactions depend both on the steric properties of the allenyl enolate and on the nature of the electrophile, and in some cases remarkable stereose-

lectivities are found (products **2b**, **7**, **9**, **12**). The regio- and stereoselectivities observed experimentally can be rationalized in terms of charge control and frontier-orbital control, of kinetic and thermodynamic control, and of steric interactions in intermediates and transition states. Thus, allenyl enolates have turned out to be a new and synthetically useful class of chiral ambident nucleophiles, and we are currently exploring furthermore the use of these compounds both from the preparative and mechanistic point of view.

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Experimental

General Information: See ref.[4a] – The NMR data for the major isomer of a mixture are marked with an asterisk (*).

Ethyl 2-Methyl-2-nonen-4-ynoate (**1c**): To a suspension of 1.50 g (50.0 mmol) of sodium hydride (80% in paraffin oil) in 100 ml of THF was added dropwise at room temp. a solution of 14.9 g (62.5 mmol) of ethyl 2-(diethoxyphosphoryl)propionate in 100 ml of THF. After the evolution of hydrogen gas had ceased (ca. 30 min) the mixture was cooled to 0°C, and a solution of crude 2-heptynal[25] [from 4.21 g (50.0 mmol) of 1-hexyne] in 100 ml of THF was added dropwise. The mixture was stirred for 1.5 h at room temp. and hydrolyzed with 100 ml of water; the organic layer was separated, and the aqueous layer was 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/pentane, 1:20) and purified further by kugelrohr distillation (100–110°C/0.05 Torr); yield: 6.43 g (66%) of **1c** as a colorless liquid. – IR: $\tilde{\nu}$ = 2200 cm^{-1} (s, C≡C), 1710 (s, C=O). – ^1H **NMR: δ = 0.93 (t, 3H, *J* = 7.3 Hz, 9-H), 1.29 (t, 3H, *J* = 7.0 Hz,** OCH_2CH_3), 1.41–1.83 (m, 4H, 7-, 8-H), 2.03 (d, 3H, *J* = 1.2 Hz, 2-CH_3), 2.42 (dt, 2H, *J* = 2.2/6.9 Hz, 6-H), 4.20 (q, 2H, *J* = 7.0 Hz, OCH_2), 6.63 (m, 1H, 3-H). – ^{13}C NMR: δ = 12.0/13.3 (2+, C-9, 2-CH_3), 14.0 (+, OCH_2CH_3), 19.3/21.7 (2–, C-7, -8), 30.4 (–, C-6), 60.4 (–, OCH_2), 77.3 (×, C-5), 103.4 (×, C-4), 120.1 (+, C-3), 137.5 (×, C-2), 167.1 (×, C-1). – MS, *m/z* (%): 194 (64) [M^+], 79 (100).

$C_{12}H_{18}O_2$ (194.3) Calcd. C 74.19 H 9.34
Found C 73.72 H 9.21

General Procedure for the Reaction of Allenyl Enolates with Electrophiles: To a suspension of copper(I) iodide in diethyl ether is added dropwise at 0°C MeLi (1.5 M solution in diethyl ether). The mixture is stirred for 15 min at 0°C, then cooled to –20°C, and a solution of the enyne **1** in diethyl ether is added dropwise. Stirring at –20°C is continued for 1 h prior to addition of the electrophile at the temp. indicated. After stirring for another 1 h at this temp. the mixture is poured into an excess of vigorously stirred 2 N H_2SO_4. The copper salts and excess of acid are removed by filtration through Celite; the filtrate is dried with $MgSO_4$ and concentrated in vacuo. If not indicated otherwise, the crude product is purified by column chromatography (SiO_2, diethyl ether/pentane, 1:10).

Ethyl (2E,4E)- and (2E,4Z)-5-Methyl-4-(2-propenyl)-2,4-nonadienoate (**2a**): From 0.86 g (4.5 mmol) of CuI in 20 ml of diethyl ether, 6.0 ml (9.0 mmol) of MeLi, 0.54 g (3.0 mmol) of **1a** in 10 ml of diethyl ether, and 1.81 g (1.3 ml, 15.0 mmol) of allyl bromide; reaction temp. –20°C. Yield: 0.42 g (60%) of **2a** [1:1 mixture of the (2*E*,4*E*) and (2*E*,4*Z*) isomers] as slightly yellow oil. – IR: $\tilde{\nu}$ = 1710 cm^{-1} (s, C=O), 1610 (s, C=C). – ^1H NMR: δ = 0.92/0.93 (2 t, 3H, 2 × *J* = 7.1 Hz, 9-H), 1.29 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3), 1.35–1.46 (m, 4H, 7-, 8-H), 1.85/1.98 (2 s, 3H, 5-CH_3), 2.17/2.36 (2 t, 2 × *J* = 7.7 Hz, 6-H), 3.00–3.04 (m, 2H, $CH_2CH=CH_2$), 4.20 (q, 2H, *J* = 7.1 Hz, OCH_2), 4.92–5.01 (m, 2H, $CH_2CH=CH_2$), 5.71–5.82 (m, 1H, $CH_2CH=CH_2$), 5.81/5.82 (2 d, 1H, 2 × *J* = 15.6 Hz, 2-H), 7.81/7.83 (2 d, 1H, 2 × *J* = 15.6 Hz, 3-H). – ^{13}C NMR: δ = 14.0/14.4 (2+, C-9, OCH_2CH_3), 19.0/20.4 (2+, 5-CH_3), 22.7/23.0 (2–, C-8), 30.3/31.3 (2–, C-7), 32.2/32.6 (2–, C-6), 34.5/35.8 (2–, $CH_2CH=CH_2$), 60.1 (–, OCH_2), 114.9/115.1 (2–, $CH_2CH=CH_2$), 115.7/116.1 (2+, $CH_2CH=CH_2$), 127.8/128.0 (2×, C-4), 135.0/135.8 (2+, C-2), 142.1/142.7 (2+, C-3), 147.6/148.0 (2×, C-5), 168.0/168.1 (2×, C-1). – MS, *m/z* (%): 236 (38) [M^+], 105 (100).

$C_{15}H_{24}O_2$ (236.4) Calcd. C 76.23 H 10.24
Found C 75.88 H 10.16

Ethyl (2E,4E)-5,6,6-Trimethyl-4-(2-propenyl)-2,4-heptadienoate (**2b**): From 0.29 g (1.5 mmol) of CuI in 10 ml of diethyl ether, 2.0 ml (3.0 mmol) of MeLi, 0.18 g (1.0 mmol) of **1b** in 10 ml of diethyl ether, and 0.60 g (0.43 ml, 5.0 mmol) of allyl bromide; reaction temp. –20°C. Yield: 0.19 g (80%) of **2b** as slightly yellow oil. – IR: $\tilde{\nu}$ = 1705 cm^{-1} (s, C=O), 1605 (s, C=C). – ^1H NMR: δ = 1.22 [s, 9H, $C(CH_3)_3$], 1.29 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3), 1.99 (s, 3H, 5-CH_3), 3.27 (d, 2H, *J* = 4.9 Hz, $CH_2CH=CH_2$), 4.19 (q, 2H, *J* = 7.1 Hz, OCH_2), 4.97 (dd, 1H, *J* = 1.8/17.2 Hz, $CH_2CH=CH_2$), 5.05 (dd, 1H, *J* = 1.8/10.3 Hz, $CH_2CH=CH_2$), 5.74–5.85 (m, 1H, **$CH_2CH=CH_2$), 5.84 (d, 1H, *J* = 15.7 Hz, 2-H), 7.87 (d, 1H, *J* =** 15.7 Hz, 3-H). – NOE difference spectra (irradiation at → intensity enhancement at): δ = 1.22 (*t*Bu) → 5.74–5.85 ($CH_2CH=CH_2$); 1.99 (5-CH_3) → 7.87 (3-H); 5.84 (2-H) → 3.27 ($CH_2CH=CH_2$); 7.87 (3-H) → 1.99 (5-CH_3). – ^{13}C NMR: δ = 14.0 (+, OCH_2CH_3), 17.8 (+, 5-CH_3), 30.4 [+, $C(CH_3)_3$], 33.6 (–, $CH_2CH=CH_2$), 37.3 [×, $C(CH_3)_3$], 59.7 (–, OCH_2), 115.6 (–, $CH_2CH=CH_2$), 116.9 (+, $CH_2CH=CH_2$), 128.3 (×, C-4), 136.3 (+, C-2), 145.1 (+, C-3), 153.1 (×, C-5), 167.6 (×, C-1). – MS, *m/z* (%): 236 (8) [M^+], 41 (100).

$C_{15}H_{24}O_2$ (236.4) Calcd. C 76.23 H 10.24
Found C 75.92 H 10.21

Ethyl 2,5-Dimethyl-3,4-nonadienoate (**3**): From 0.29 g (1.5 mmol) of CuI in 10 ml of diethyl ether, 2.0 ml (3.0 mmol) of MeLi, 0.18 g (1.0 mmol) of **1a** in 10 ml of diethyl ether, and 0.46 g (0.3 ml, 2.8 mmol) of methyl triflate; addition of the triflate at –100°C, warming up to –20°C in 2 h prior to workup. Yield: 0.15 g (71%) of **3** as slightly yellow oil (1:1 mixture of diastereomers). – IR: $\tilde{\nu}$ = 1960 cm^{-1} (m, C=C=C), 1730 (s, C=O). – ^1H NMR: δ = 0.90 (t, 3H, *J* = 7.1 Hz, 9-H), 1.21–1.29 (m, 6H, 2-CH_3, OCH_2CH_3), 1.31–1.45 (m, 4H, 7-, 8-H), 1.68 (d, 3H, *J* = 2.8 Hz, 5-CH_3), 1.91–1.97 (m, 2H, 6-H), 3.06 (m, 1H, 2-H), 4.14 (q, 2H, *J* = 7.2 Hz, OCH_2), 5.19 (dq, 1H, *J* = 5.2/2.8 Hz, 3-H). – ^{13}C NMR: δ = 13.9/**14.1 (2+, C-9, OCH_2CH_3), 16.5 (+, 2-CH_3), 19.0 (+, 5-CH_3), 22.3** (–, C-8), 26.6 (–, C-7), 33.5 (–, C-6), 39.8 (+, C-2), 60.4 (–, OCH_2), 90.6 (+, C-3), 102.2 (×, C-5), 174.8 (×, C-1), 200.9 (×, C-4). – MS, *m/z* (%): 210 (27) [M^+], 95 (100).

$C_{13}H_{22}O_2$ (210.3) Calcd. C 74.24 H 10.54
Found C 74.07 H 10.84

Ethyl 2,5,6,6-Tetramethyl-3,4-heptadienoate (**4**): From 1.43 g (7.5 mmol) of CuI in 30 ml of diethyl ether, 10.0 ml (15.0 mmol) of MeLi, 0.90 g (5.0 mmol) of **1b** in 10 ml of diethyl ether, and 4.10 g (2.8 ml, 25.0 mmol) of methyl triflate; addition of the triflate at –100°C, warming up to –20°C in 2 h prior to workup. Yield: 0.54 g (51%) of **4** as slightly yellow oil (1:1 mixture of diastereomers). – IR: $\tilde{\nu}$ = 1960 cm^{-1} (m, C=C=C), 1730 (s, C=O). – ^1H NMR: δ =

1.04 [s, 9H, $C(CH_3)_3$], 1.20–1.28 (m, 6H, 2-CH_3, OCH_2CH_3), 1.69 (d, 3H, J = 2.7 Hz, 5-CH_3), 3.06 (m, 1H, 2-H), 4.13 (q, 2H, J = 7.2 Hz, OCH_2), 5.19 (m, 1H, 3-H). – ^{13}C NMR: δ = 14.1 (+, OCH_2CH_3), 14.8 (+, 5-CH_3), 16.1/16.2 (2+, 2-CH_3), 28.9 [+, $C(CH_3)_3$], 33.2 (×, C-6), 42.7 (+, C-2), 60.5 (–, OCH_2), 97.0 (+, C-3), 103.0 (×, C-5), 176.1 (×, C-1), 200.1 (×, C-4). – MS, *m/z* (%): 210 (17) [M^+], 57 (100).

$C_{13}H_{22}O_2$ (210.3) Calcd. C 74.24 H 10.54
Found C 73.78 H 10.47

Ethyl 2,2,5-Trimethyl-3,4-nonadienoate (**5**): From 0.29 g (1.5 mmol) of CuI in 10 ml of diethyl ether, 2.0 ml (3.0 mmol) of MeLi, 0.19 g (1.0 mmol) of **1c** in 10 ml of diethyl ether, and 0.46 g (0.3 ml, 2.8 mmol) of methyl triflate; addition of the triflate at –100°C, warming up to –20°C in 2 h prior to workup. Yield: 0.18 g (80%) of **5** as slightly yellow oil. – IR: $\tilde{\nu}$ = 1960 cm^{-1} (m, C=C=C), 1720 (s, C=O). – ^1H NMR: δ = 0.89 (t, 3H J = 7.1 Hz, 9-H), 1.25 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 1.26 (s, 6H, 2-CH_3), 1.28–1.43 (m, 4H, 7-, 8-H), 1.68 (d, 3H, J = 2.8 Hz, 5-CH_3), 1.91–1.97 (m, 2H, 6-H), 4.12 (q, 2H, J = 7.2 Hz, OCH_2), 5.28 (q, 1H, J = 2.8 Hz, 3-H). – ^{13}C NMR: δ = 13.9/14.1 (2+, C-9, OCH_2CH_3), 19.1 (+, 5-CH_3), 22.4 (–, C-8), 25.5 (+, 2-CH_3), 29.7 (–, C-7), 33.7 (–, C-6), 42.7 (×, C-2), 60.5 (–, OCH_2), 97.0 (+, C-3), 103.0 (×, C-5), 176.7 (×, C-1), 199.6 (×, C-4). – MS; *m/z* (%): 224 (22) [M^+], 181 (100).

$C_{14}H_{24}O_2$ (224.3) Calcd. C 74.95 H 10.78
Found C 74.17 H 11.04

Ethyl 2-(α-Hydroxybenzyl)-5-methyl-3,4-nonadienoate (**6**): From 1.43 g (7.5 mmol) of CuI in 30 ml of diethyl ether, 10.0 ml (15.0 mmol) of MeLi, 0.90 g (5.0 mmol) of **1a** in 10 ml of diethyl ether, and 2.65 g (2.5 ml, 25.0 mmol) of benzaldehyde; reaction temp. –20°C. The crude product was separated into two fractions by column chromatography (SiO_2, diethyl ether/pentane, 1:2) yielding 0.47 g (31%, Fr. 1) and 0.72 g (48%, Fr. 2) of **6** as slightly yellow oils (each fraction consists of 1:1 mixtures of two diastereomers). – IR: $\tilde{\nu}$ = 3600–3200 cm^{-1} (s, OH), 1960 (m, C=C=C), 1720 (s, C=O). – ^1H NMR: Fr. 1: δ = 0.84–0.91 (m, 3H, 9-H), 1.17 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 1.21–1.40 (m, 4H, 7-, 8-H), 1.49/1.67 (2 d, 3H, 2 × J = 2.7 Hz, 5-CH_3), 1.79–1.91 (m, 2H, 6-H), 3.22–3.30 (m, 2H, 2-H, OH), 4.09 (q, 2H, J = 7.1 Hz, OCH_2), 5.05 (d, 1H, J = 5.2 Hz, CHPhOH), 5.17 (dq, 1H, J = 5.6/2.7 Hz, 3-H), 7.23–7.42 (m, 5H, Ph). Fr. 2: δ = 0.81–0.91 (m, 3H, 9-H), 1.11–1.33 (m, 4H, 7-, 8-H), 1.26 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 1.34/1.59 (2 d, 3H, 2 × J = 2.8 Hz, 5-CH_3), 1.70–1.85 (m, 2H, 6-H), 3.13 (s, 1H, OH), 3.34/3.35 (2 t, 1H, 2 × J = 8.6 Hz, 2-H), 4.07 (q, 2H, J = 7.2 Hz, OCH_2), 4.88–4.93 (m, 2H, 3-H, CHPhOH), 7.27–7.36 (m, 5H, Ph). – ^{13}C NMR: Fr. 1: δ = 13.9/14.0/14.1 (3+, C-9, OCH_2CH_3), 18.4/18.7 (2+, 5-CH_3), 22.3 (–, C-8), 29.4 (–, C-7), 33.3/33.4 (2–, C-6), 54.3/54.5 (2+, C-2), 60.8 (–, OCH_2), 73.7/73.8 (2+, CHPhOH), 84.4/84.7 (2+, C-3), 101.4/101.6 (2×, C-5), 126.4/126.9/127.6/127.9/128.1/128.3 (6+, Ph), 140.0/141.5 (2×, Ph), 173.1 (×, C-1), 203.5/203.6 (2×, C-4). Fr. 2: δ = 13.8/13.9/14.1 (3+, C-9, OCH_2CH_3), 18.4/18.6 (2+, 5-CH_3), 22.2 (–, C-8), 29.2/29.4 (2–, C-7), 33.2 (–, C-6), 54.1/54.4 (2+, C-2), 60.8 (–, OCH_2), 75.4/75.5 (2+, CHPhOH), 85.8/86.0 (2+, C-3), 101.7/101.8 (2×, C-5), 125.3/126.9/127.3/127.8/128.2/128.4 (6+, Ph), 141.4 (×, Ph), 173.3 (×, C-1), 202.7/202.8 (2×, C-4). – MS, *m/z* (%): 302 (6) [M^+], 195 (100).

$C_{19}H_{26}O_3$ (302.4) Calcd. C 75.46 H 8.67
Found C 75.45 H 8.66

Ethyl 2-(α-Hydroxybenzyl)-5,6,6-trimethyl-3,4-heptadienoate (**7**): From 2.86 g (15.0 mmol) of CuI in 40 ml of diethyl ether, 20.0 ml (30.0 mmol) of MeLi, 1.80 g (10.0 mmol) of **1b** in 20 ml of diethyl ether, and 2.12 g (2.0 ml, 20.0 mmol) of benzaldehyde; reaction temp. –20°C. The product consists of four diastereomers in the ratio of 8:8:4:1; it was separated into two pairs of diastereomers by column chromatography (SiO_2, diethyl ether/hexane, 1:2): Fr. 1: 0.48 g (16%), colorless oil, Fr. 2: 2.51 g (83%) colorless crystals (m.p. 77–78°C). – IR: $\tilde{\nu}$ = 3600–3200 cm^{-1} (s, OH), 1960 (m, C=C=C), 1720 (s, C=O). – ^1H NMR: Fr. 1: δ = 0.93/1.02* [2 s, 9H, $C(CH_3)_3$], 1.16 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 1.49*/1.68 (2 d, 3H, 2 × J = 2.8 Hz, 5-CH_3), 3.00 (s, 1H, OH), 3.26 (dd, 1H, J = 5.2/8.4 Hz, 2-H), 4.07/4.08* (2 q, 2H, 2 × J = 7.1 Hz, OCH_2), 5.05/5.06* (2 d, 1H, 2 × J = 5.2 Hz, CHPhOH), 5.14 (dq, 1H, J = 8.4/2.8 Hz, 3-H), 7.20–7.40 (m, 5H, Ph). Fr. 2: δ = 0.87/0.99 [2 s, 9H, $C(CH_3)_3$], 1.25/1.26 (2 t, 3H, 2 × J = 7.1 Hz, OCH_2CH_3), 1.35/1.57 (2 d, 3H, 2 × J = 2.8 Hz, 5-CH_3), 3.00 (s, 1H, OH), 3.33 (t, J = 8.4 Hz)/3.37 (dd, J = 7.8/8.7 Hz, 1H, 2-H), 4.12–4.24 (m, 2H, OCH_2), 4.80–4.96 (m, 2H, 3-H, CHPhOH), 7.20–7.40 (m, 5H, Ph). – ^{13}C NMR: Fr. 1: δ = 14.0/14.7/15.0 (3+, 5-CH_3, OCH_2CH_3), 28.8*/28.9 [2+, $C(CH_3)_3$], 33.4 (×, C-6), 54.3/54.5* (2+, C-2), 60.7 (–, OCH_2), 73.7 (+, CHPhOH), 84.8 (+, C-3), 110.4*/110.5 (2×, C-5), 126.4/127.6/128.1/128.2/129.0/129.8 (6+, Ph), 140.8 (×, Ph), 173.4*/173.5 (2×, C-1), 202.0/202.7* (2×, C-4). Fr. 2: δ = 14.0/14.2/14.7 (3+, 5-CH_3, OCH_2CH_3), 28.6/28.8 [2+, $C(CH_3)_3$], 33.2 (×, C-6), 53.7/54.6 (2+, C-2), 60.7 (–, OCH_2), 75.2/75.4 (2+, CHPhOH), 86.1/86.2 (2+, C-3), 110.5/110.9 (2×, C-5), 126.7/126.8/127.7/127.8/128.2/128.3 (6+, Ph), 141.3 (×, Ph), 173.1/173.3 (2×, C-1), 201.5/201.7 (2×, C-4). – MS, *m/z* (%): 302 (5) [M^+], 195 (100).

$C_{19}H_{26}O_3$ (302.4) Calcd. C 75.46 H 8.67
Found C 75.39 H 8.71

Ethyl 2-(α-Hydroxybenzyl)-2,5-dimethyl-3,4-nonadienoate (**8**): From 0.86 g (4.5 mmol) of CuI in 20 ml of diethyl ether, 6.0 ml (9.0 mmol) of MeLi, 0.58 g (3.0 mmol) of **1c** in 10 ml of diethyl ether, and 1.59 g (1.5 ml, 15.0 mmol) of benzaldehyde; reaction temp. –20°C. The crude product was separated into two fractions by column chromatography (SiO_2, diethyl ether/pentane, 1:5) yielding 0.29 g (31%, Fr. 1) and 0.29 g (31%, Fr. 2) of **8** as slightly yellow oils (each fraction consists of 1:1 mixtures of two diastereomers). – IR: $\tilde{\nu}$ = 3600–3200 cm^{-1} (s, OH), 1965 (m, C=C=C), 1710 (s, C=O). – ^1H NMR: Fr. 1: δ = 0.84/0.88 (2 t, 3H, 2 × J = 7.3 Hz, 9-H), 1.03/1.05 (2 s, 3H, 2-CH_3), 1.26 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 1.12–1.47 (m, 4H, 7-, 8-H), 1.49/1.66 (2 d, 3H, 2 × J = 2.8 Hz, 5-CH_3), 1.73–1.94 (m, 2H, 6-H), 3.27 (s, 1H, OH), 4.13 (q, 2H, J = 7.2 Hz, OCH_2), 5.00 (s, 1H, CHPhOH), 5.46 (q, 1H, J = 2.8 Hz, 3-H), 7.23–7.35 (m, 5H, Ph). Fr. 2: δ = 0.80/0.88 (2 t, 3H, 2 × J = 7.1 Hz, 9-H), 1.00–1.37 (m, 4H, 7-, 8-H), 1.10/1.11 (2 s, 3H, 2-CH_3), 1.25/1.26 (2 t, 3H, 2 × J = 7.1 Hz, OCH_2CH_3), 1.39/1.63 (2 d, 3H, 2 × J = 2.8 Hz, 5-CH_3), 1.65–1.90 (m, 2H, 6-H), 3.17 (s, 1H, OH), 4.17 (q, 2H, J = 7.1 Hz, OCH_2), 5.00 (s, 1H, CHPhOH), 5.18 (q, 1H, J = 2.8 Hz, 3-H), 7.13–7.33 (m, 5H, Ph). – ^{13}C NMR: Fr. 1: δ = 13.8/14.0 (2+, C-9, OCH_2CH_3), 18.2/18.5/18.7 (3+, 2-CH_3, 5-CH_3), 22.3 (–, C-8), 29.5/29.6 (2–, C-7), 33.4 (–, C-6), 52.4/52.5 (2×, C-2), 61.0 (–, OCH_2), 78.2 (+, CHPhOH), 91.1/93.2 (2+, C-3), 103.0/103.2 (2×, C-5), 127.4/127.5/127.7/127.8/127.9 (5+, Ph), 139.4 (×, Ph), 175.8/175.9 (2×, C-1), 202.1 (×, C-4). Fr. 2: δ = 13.4/13.9 (2+, C-9, OCH_2CH_3), 15.7 (+, 2-CH_3), 18.3/18.6 (2+, 5-CH_3), 22.1/22.3 (2–, C-8), 29.5/29.6 (2–, C-7), 33.2/33.3 (2–, C-6), 52.6 (×, C-2), 60.9 (–, OCH_2), 78.1/78.2 (2+, CHPhOH), 92.9/93.2 (2+, C-3), 103.1/103.2 (2×, C-5), 126.9/127.2/127.3/127.4/127.6/127.8 (6+, Ph), 139.7 (×, Ph), 175.4/175.6 (2×, C-1), 201.0/201.1 (2×, C-4). – MS, *m/z* (%): 316 (25) [M^+], 274 (100).

$C_{20}H_{28}O_3$ (316.4) Calcd. C 75.91 H 8.92
Found C 75.77 H 8.67

Ethyl 2-(1-Hydroxy-2,2-dimethylpropyl)-5,6,6-trimethyl-3,4-heptadienoate (**9**): From 2.86 g (15.0 mmol) of CuI in 40 ml of diethyl

ether, 20.0 ml (30.0 mmol) of MeLi, 1.80 g (10.0 mmol) of **1b** in 20 ml of diethyl ether, and 1.72 g (2.2 ml, 20.0 mmol) of pivalic aldehyde; reaction temp. −20°C. The crude product was purified by column chromatography (SiO_2, diethyl ether/hexane, 1:2) yield: 2.30 g (82%) of **9** as colorless liquid (1:1 mixture of diastereomers). – IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 1960 (m, C=C=C), 1710 (s, C=O). – ^1H NMR: δ = 0.92/0.94 [2 s, 9H, CHOHC(CH_3)$_3$], 1.04 [s, 9H, 5-C(CH_3)$_3$], 1.27/1.28 (2 t, 3H, 2 × *J* = 7.1 Hz, OCH_2CH_3), 1.68/1.69 (2 d, 3H, 2 × *J* = 2.9 Hz, 5-CH_3), 3.21/3.23 (2 t, 1H, *J* = 3.0/3.6 Hz, 2-H), 3.39/3.42 (2 d, 1H, *J* = 3.0/3.6 Hz, CHOH), 4.14/4.15 (2 q, 2H, 2 × *J* = 7.1 Hz, OCH_2), 5.24 (m, 1H, 3-H). – ^{13}C NMR: δ = 13.8/14.3/14.6 (3+, 5-CH_3, OCH_2CH_3), 26.0/26.1 [2+, CHOHC(CH_3)$_3$], 28.6/28.7 [2+, 5-C(CH_3)$_3$], 33.3 (×, C-6), 35.7 (×, CHOHC(CH_3)$_3$), 45.8/46.7 (2+, C-2), 60.5 (−, OCH_2), 81.0/81.4 (2+, CHOH), 89.0/89.1 (2+, C-3), 110.7/111.0 (2×, C-5), 174.4 (×, C-1), 200.5/200.6 (2×, C-4). – MS, *m/z* (%): 282 (3) [M^+], 57 (100).

$C_{17}H_{30}O_3$ (282.4) Calcd. C 72.30 H 10.71
Found C 72.01 H 10.73

Ethyl 2-(1-Hydroxy-2-propenyl)-5-methyl-3,4-nonadienoate (**10**): From 0.86 g (4.5 mmol) of CuI in 20 ml of diethyl ether, 6.0 ml (9.0 mmol) of MeLi, 0.54 g (3.0 mmol) of **1a** in 10 ml of diethyl ether, and 0.84 g (1.0 ml, 15.0 mmol) of acrolein; reaction temp. −20°C. The crude product was separated into two fractions by column chromatography (SiO_2, diethyl ether/pentane, 1:5); yield: 0.19 g (25%, Fr. 1) and 0.21 g (28%, Fr. 2) of **10** as slightly yellow oils (each fraction consists of 1:1 mixtures of two diastereomers). – IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 1960 (m, C=C=C), 1740 (s, C=O). – ^1H NMR: Fr. 1: δ = 0.89/0.90 (2 t, 3H, 2 × *J* = 7.0 Hz, 9-H), 1.27 (t, 3H, *J* = 7.0 Hz, OCH_2CH_3), 1.31−1.45 (m, 4H, 7-, 8-H), 1.69 (d, 3H, *J* = 2.8 Hz, 5-CH_3), 1.92−1.97 (m, 2H, 6-H), 2.90 (s, 1H, OH), 3.11 (dd, 1H, *J* = 5.2/5.3 Hz, 2-H), 4.17 (q, 2H, *J* = 7.0 Hz, OCH_2), 4.43 (m, 1H, CHOH), 5.15−5.21 (m, 1H, 3-H), 5.20 (dd, 1H, *J* = 1.5/10.7 Hz, CH=CH_2), 5.34 (dd, 1H, *J* = 1.5/17.8 Hz, CH=CH_2), 5.82−5.85 (m, 1H, CH=CH_2). Fr. 2: δ = 0.89/0.90 (2 t, 3H, 2 × *J* = 7.1 Hz, 9-H), 1.25 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3), 1.30−1.43 (m, 4H, 7-, 8-H), 1.67 (d, 3H, *J* = 2.7 Hz, 5-CH_3), 1.91−1.93 (m, 2H, 6-H), 2.96 (s, 1H, OH), 3.03−3.10 (m, 1H, 2-H), 4.17 (q, 2H, *J* = 7.1 Hz, OCH_2), 4.35 (m, 1H, CHOH), 5.07 (dq, 1H, *J* = 5.4/2.7 Hz, 3-H), 5.20 (dd, 1H, *J* = 1.2/10.6 Hz, CH=CH_2), 5.33 (dd, 1H, *J* = 1.2/17.1 Hz, CH=CH_2), 5.85−6.00 (m, 1H, CH=CH_2). – ^{13}C NMR: Fr. 1: δ = 13.9/14.1 (2+, C-9, OCH_2CH_3), 18.8/19.1 (2+, 5-CH_3), 22.3 (−, C-8), 29.5/29.7 (2−, C-7), 33.4/33.6 (2−, C-6), 52.3/52.4 (2+, C-2), 60.9 (−, OCH_2), 72.9 (+, CHOH), 84.6/84.7 (2+, C-3), 101.6/101.7 (2×, C-5), 116.5 (−, CH=CH_2), 137.3 (+, CH=CH_2), 172.9 (×, C-1), 203.3 (×, C-4). Fr. 2: δ = 13.8/14.1 (2+, C-9, OCH_2CH_3), 18.7/18.8 (2+, 5-CH_3), 22.3 (−, C-8), 29.3/29.5 (2−, C-7), 33.3/33.5 (2−, C-6), 52.4/52.6 (2+, C-2), 60.7 (−, OCH_2), 73.5 (+, CHOH), 85.8/85.9 (2+, C-3), 101.7 (×, C-5), 116.2 (−, CH=CH_2), 138.0 (+, CH=CH_2), 172.9 (×, C-1), 202.7 (×, C-4). – MS; *m/z* (%): 252 (3) [M^+], 167 (100).

$C_{15}H_{24}O_3$ (252.4) Calcd. C 71.39 H 9.59
Found C 71.02 H 9.67

Ethyl 2-(1-Hydroxy-1-methylethyl)-5-methyl-3,4-nonadienoate (**11**): From 0.29 g (1.5 mmol) of CuI in 10 ml of diethyl ether, 2.0 ml (3.0 mmol) of McLi, 0.18 g (1.0 mmol) of **1a** in 10 ml of diethyl ether, and 0.29 g (0.4 ml, 5.0 mmol) of acetone; reaction temp. −20°C. Yield: 0.18 g (71%) of **11** as slightly yellow oil (1:1 mixture of diastereomers). – IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 1965 (m, C=C=C), 1705 (s, C=O). – ^1H NMR: δ = 0.89 (t, 3H, *J* = 7.0 Hz, 9-H), 1.25−1.53 [m, 13H, 7-, 8-H, C(CH_3)$_2$OH, OCH_2CH_3], 1.67−1.71 (m, 3H, 5-CH_3), 1.91−1.98 (m, 2H, 6-H), 2.94/2.95 (2 d, 1H, 2 × *J* = 9.3 Hz, 2-H), 3.34 (s, 1H, OH), 4.19 (q, 2H, *J* = 7.2 Hz, OCH_2), 5.22 (dq, 1H, *J* = 9.3/2.9 Hz, 3-H). – ^{13}C NMR: δ = 13.7/13.9 (2+, C-9, OCH_2CH_3), 18.6/18.7 (2+, 5-CH_3), 22.1 (−, C-8), 26.2/26.4/28.4 (3+, C(CH_3)$_2$OH), 29.3/29.5 (2−, C-7), 33.1/33.4 (2−, C-6), 56.4/56.6 (2+, C-2), 60.5 (−, OCH_2), 71.0/71.1 [2×, C(CH_3)$_2$OH], 85.4/85.7 (2+, C-3), 100.5/101.6 (2×, C-5), 174.0 (×, C-1), 203.1 (×, C-4). – MS, *m/z* (%): 254 (2) [M^+], 44 (100).

$C_{15}H_{26}O_3$ (254.4) Calcd. C 70.83 H 10.30
Found C 69.65 H 10.49

Ethyl 2-(1-Hydroxy-1-methylethyl)-5,6,6-trimethyl-3,4-heptadienoate (**12**): From 1.43 g (7.5 mmol) of CuI in 20 ml of diethyl ether, 10.0 ml (15.0 mmol) of MeLi, 0.90 g (5.0 mmol) of **1b** in 20 ml of diethyl ether, and 1.45 g (1.8 ml, 25.0 mmol) of acetone; reaction temp. −20°C. The crude product was purified by kugelrohr distillation (90−100°C/0.06 mbar); yield: 1.06 g (83%) of **12** as colorless oil (4:1 mixture of diastereomers). – IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 1960 (m, C=C=C), 1725 (s, C=O). – ^1H NMR: δ = 1.04*/1.05 [2 s, 9H, C(CH_3)$_3$], 1.24/1.26/1.27 [3 s, 6H, C(CH_3)$_2$OH], 1.28*/1.29 (2 t, 3H, 2 × *J* = 7.1 Hz, OCH_2CH_3), 1.68/1.69* (2 d, 3H, *J* = 2.6/2.8 Hz, 5-CH_3), 2.93*/2.94 (2 d, 1H, *J* = 9.3/9.1 Hz, 2-H), 3.42 (s, 1H, OH), 4.18*/4.19 (2 q, 2H, 2 × *J* = 7.1 Hz, OCH_2), 5.19*/5.22 (2 dq, 1H, 2 × *J* = 9.4/2.8 Hz, 3-H). – ^{13}C NMR: δ = 14.2 (+, OCH_2CH_3), 14.9*/15.0 (2+, 5-CH_3); 26.5*/26.9/28.7*/29.4 [4+, C(CH_3)$_2$OH], 28.9*/29.1 [2+, C(CH_3)$_3$], 33.4 (×, C-6), 56.6/56.9* (2+, C-2), 60.7 (−, OCH_2), 71.3 [×, C(CH_3)$_2$OH], 85.8/86.0* (2+, C-3), 116.1 (×, C-5), 174.5 (×, C-1), 202.4 (×, C-4). – MS, *m/z* (%): 254 (<1) [M^+], 59 (100).

$C_{15}H_{26}O_3$ (254.4) Calcd. C 70.83 H 10.30
Found C 70.49 H 10.32

(E)- and (Z)-6-Methyl-2-(trimethylsilyloxy)-2,4,5-decatriene (**14**): From 0.57 g (3.0 mmol) of CuI in 15 ml of diethyl ether, 4.0 ml (6.0 mmol) of MeLi, 0.30 g (2.0 mmol) of **1d** in 10 ml of diethyl ether; 1.63 g (1.9 ml, 15.0 mmol) of chlorotrimethylsilane and 1.52 g (2.1 ml, 15.0 mmol) of triethylamine were added at −80°C, the mixture was warmed up to room temp., stirred for 30 min and poured onto ice. Filtration through celite was followed by concentration in vacuo and purification by column chromatography (SiO_2, diethyl ether/pentane, 1:10). Yield: 0.36 g (76%) of **14** [1:2 mixture of (*E*) and (*Z*) isomers] as slightly yellow oil. – ^1H NMR: δ = 0.20/0.22* [2 s, 9H, Si(CH_3)$_3$], 0.89 (t, 3H, *J* = 7.0 Hz, 10-H), 1.26−1.44 (m, 4H, 8-, 9-H), 1.67/1.68* (2 s, 3H, 1-H), 1.81−1.83 (m, 3H, 6-CH_3), 1.87−1.97 (m, 2H, 7-H), 4.97*/5.12 (2 d, 1H, 2 × *J* = 10.7 Hz, 3-H), 5.70−5.93* (2 dq, 1H, 2 × *J* = 10.7/2.9 Hz, 4-H). – NOE difference spectra (irradiation at → intensity enhancement at): δ = 0.20/0.22* [Si(CH_3)$_3$] → 5.12 (3-H), 5.93* (4-H); 1.81−1.83 (6-CH_3) → 4.97* (3-H), 5.70 (4-H); 4.97* (3-H) → 1.81−1.83 (6-CH_3).

[1] [1a] H. Stetter, *Methoden der Organischen Chemie (Houben-Weyl)*, 4th Ed.; vol.7/2b, Thieme, Stuttgart, **1976**, p. 1385. – [1b] J. D'Angelo, *Tetrahedron* **1976**, *32*, 2979−2990. – [1c] L. M. Jackman, B. C. Lange, *Tetrahedron* **1977**, *33*, 2737−2769. – [1d] E. M. Kaiser, J. D. Petty, P. L. A. Knutson, *Synthesis* **1977**, 509−550. – [1e] N. Petragnani, M. Yonashiro, *Synthesis* **1982**, 521−578. – [1f] S. Arseniyadis, K. S. Kyler, D. S. Watt, *Org. React.* **1984**, *31*, 1−364.

[2] [2a] R. J. K. Taylor, *Synthesis* **1985**, 364−392. – [2b] M. J. Chapdelaine, M. Hulce, *Org. React.* **1990**, *38*, 225−653.

[3] [3a] Ref. [1a], pp. 1408−1412. – [3b] H. Ahlbrecht, D. Liesching, *Synthesis* **1976**, 746−748. – [3c] W. Oppolzer, L. Bieber, E. Francotte, *Tetrahedron Lett.* **1979**, 981−984. – [3d] K. Takabe, N. Nagaoka, T. Endo, T. Katagiri, *Chem. Ind. (London)* **1981**, 540−541. – [3e] E. Vedejs, D. M. Gapinski, *Tetrahedron Lett.* **1981**, *22*, 4913−4916. – [3f] D. Hoppe, *Nachr. Chem. Tech. Lab.* **1982**, *30*, 196−198. – [3g] M. Yamashita, K. Matsumiya, K. Nakano, R. Suemitsu, *Chem. Lett.* **1988**, 1215−1218. – [3h] Y. Yamamoto, S. Hatsuya, J. Yamada, *Tetrahedron Lett.* **1989**, *30*,

3445–3448. — [3i] C. Unger, R. Zimmer, H.-U. Reißig, E.-U. Würthwein, *Chem. Ber.* **1991**, *124*, 2279–2287.

[4] [4a]N. Krause, *Chem. Ber.* **1990**, *123*, 2173–2180. — [4b] S. Arndt, Diploma Thesis, Technische Hochschule Darmstadt, **1991**.

[5] [5a] N. Krause, *Chem. Ber.* **1991**, *124*, 2633–2635. — [5b] N. Krause, G. Handke, *Tetrahedron Lett.* **1991**, *32*, 7125–7228. — [5c] N. Krause, G. Handke, *Tetrahedron Lett.* **1991**, *32*, 7229–7232. — [5d] M. Cheng, M. Hulce, *J. Org. Chem.* **1990**, *55*, 964–975.

[6] In contrast to our findings, the reaction of allenyl enolates obtained from 3-ethynyl-2-cycloalkenones with electrophiles was found to proceed with limited regiocontrol: S. Lee, M. Shih, M. Hulce, *Tetrahedron Lett.* **1992**, *33*, 185–188.

[7] N. Krause, *J. Org. Chem.* **1992**, *57*, 3509–3512.

[8] In order to represent the geometry of allenes correctly and to facilitate the discussion of the stereochemical course of their reactions, steric formulae of type **B** are used throughout this paper; here, one enantiomer is shown arbitrarily although all reaction sequences were conducted with racemic materials.

[9] [9a] P. v. R. Schleyer, *Pure Appl. Chem.* **1984**, *56*, 151–162. — [9b] D. Seebach, *Angew. Chem.* **1988**, *100*, 1685–1715; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624–1654. — [9c] W. Zarges, M. Marsch, K. Harms, W. Koch, G. Frenking, G. Boche, *Chem. Ber.* **1991**, *124*, 543–549. — [9d] W. Zarges, M. Marsch, K. Harms, F. Haller, G. Frenking, G. Boche, *Chem. Ber.* **1991**, *124*, 861–866.

[10] **1a**: N. Petragnani, T. J. Brocksom, A. R. Gato, *Farmaceo, Ed. Sci.* **1977**, *32*, 627–634; *Chem. Abstr.* **1977**, *87*, 167504a; **1b**: T. R. Boronoeva, N. N. Belyaev, M. D. Stadnichuk, A. A. Petrov, *Zh. Obshch. Khim.* **1974**, *44*, 1949–1958; *J. Gen. Chem. USSR* **1974**, *44*, 1914–1921; *Chem. Abstr.* **1975**, *82*, 43506e; **1c**: see Experimental Section; **1d**: G. A. Molander, H. C. Brown, *J. Org. Chem.* **1977**, *42*, 3106–3108.

[11] [11a] R. A. Amos, J. A. Katzenellenbogen, *J. Org. Chem.* **1978**, *43*, 555–560. — [11b] S. Tsuboi, T. Masuda, A. Takeda, *J. Org. Chem.* **1982**, *47*, 4478–4482.

[12] The base-catalyzed isomerization of ethyl 5,6,6-trimethyl-3,4-heptadienoate with EtONa/EtOH yields a 2:1 mixture of ethyl (2*E*,4*Z*)- and (2*E*,4*E*)-5,6,6-dimethyl-2,4-heptadienoate, i.e. protonation from the sterically less hindered side of the enolate predominates; in contrast, isomerization of the allenic ester with $BF_3 \cdot Et_2O/CH_2Cl_2$ gives the thermodynamically preferred 2*E*,4*E*-isomer exclusively.

[13] H. Günther, *NMR-Spektroskopie*, Thieme-Verlag, Stuttgart, 2nd Ed., **1983**.

[14] [14a] J. P. Marino, R. J. Linderman, *J. Org. Chem.* **1981**, *46*, 3696–3702. — [14b] I. Fleming, D. A. Perry, *Tetrahedron* **1981**, *37*, 4027–4034. — [14c] P. Brownbridge, *Synthesis* **1983**, 1–28 and 85–104.

[15] W. J. Scott, J. E. McMurry, *Acc. Chem. Res.* **1988**, *21*, 47–54.

[16] N. Krause, S. Arndt, *Chem. Ber.* **1993**, *126*, 261–263, following paper.

[17] I. Fleming, *Grenzorbitale und Reaktionen organischer Verbindungen*, Verlag Chemie, Weinheim, **1979**.

[18] MNDO version 4.01: M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

[19] Cf. H. E. Zimmerman, *Acc. Chem. Res.* **1987**, *20*, 263–268, and literature cited therein.

[20] C. H. Heathcock, in *Comprehensive Organic Synthesis*, vol. 2 (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, pp. 133-179.

[21] [21a] R. A. Gibbs, K. Bartels, R. W. K. Lee, W. H. Okamura, *J. Am. Chem. Soc.* **1989**, *111*, 3717–3825. — [21b] N. Krause, unpublished results.

[22] [22a] A. S. Cieplak, *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552. — [22b] C. R. Johnson, B. D. Tait, A. S. Cieplak, *J. Am. Chem. Soc.* **1987**, *109*, 5875–5876. — [22c] W. Chung, N. J. Turro, S. Srivastava, H. Li, W. J. le Noble, *J. Am. Chem. Soc.* **1988**, *110*, 7882–7883. — [22d] A. M. Naperstkow, J. B. Macaulay, M. J. Newlands, A. G. Fallis, *Tetrahedron Lett.* **1989**, *30*, 5077–5080. — [22e] W. R. Dolbier, Jr., *Acc. Chem. Res.* **1991**, *24*, 63–69. — [22f] J. M. Coxon, D. Q. McDonald, *Tetrahedron Lett.* **1992**, *33*, 651–654. — [22g] J. M. Hahn, W. J. le Noble, *J. Am. Chem. Soc.* **1992**, *114*, 1916–1917.

[23] [23a] J. W. Baker, *Hyperconjugation*, Oxford University Press, London, **1952**. — [23b] M. J. S. Dewar, *Hyperconjugation*, Ronald Press, New York, **1962**.

[24] Reviews: [24a] C. H. Heathcock in *Asymmetric Synthesis*, vol. 3 (Ed.: J. D. Morrison), Academic Press, Orlando, **1984**, pp. 111–212. — [24b] C. H. Heathcock in *Comprehensive Organic Synthesis*, vol. 2 (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, pp 181–238.

[25] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 2nd Ed., **1988**, pp. 102–103.

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CAS Registry Numbers

1a: 64576-91-6 / **1b**: 54599-49-4 / **1c**: 143237-67-6 / **1d**: 63922-98-5 / **2a** (*E,E*): 143237-40-5 / **2a** (*Z,E*): 143237-41-6 / **2b** (*E,E*): 143237-42-7 / **3** (*R*): 143193-04-8 / **3** (*S*): 143289-16-1 / **4** (*R*): 143290-25-9 / **4** (*S*): 143215-14-9 / **5**: 143237-43-8 / **6** (*R-R*,R**): 143237-46-1 / **6** (*R-R*,S**): 143237-45-0 / **6** (*S-R*,R**): 143237-47-2 / **6** (*S-R*,S**): 143237-44-9 / **7** (*R-R*,R**): 143237-50-7 / **7** (*R-R*,S**): 143237-49-4 / **7** (*S-R*,R**): 143237-51-8 / **7** (*S-R*,S**): 143237-48-3 / **8** (*R-R*,R**): 143237-52-9 / **8** (*R-R*,S**): 143237-54-1 / **8** (*S-R*,R**): 143237-53-0 / **8** (*S-R*,S**): 143265-77-4 / **9** (*R*,R**): 143237-56-3 / **9** (*R*,S**): 143237-55-2 / **10** (*R-R*,R**): 143237-57-4 / **10** (*R-R*,S**): 143237-59-6 / **10** (*S-R*,R**): 143237-58-5 / **10** (*S-R*,S**): 143237-60-9 / **11** (*R*): 143237-61-0 / **11** (*S*): 143237-62-1 / **12** (*R*): 143237-63-2 / **12** (*S*): 143237-64-3 / **14** (*E*): 143237-65-4 / **14** (*Z*): 143237-66-5 / (diethoxyphosphoryl)propionate: 3699-66-9 / 2-heptynal: 1846-67-9 / allyl bromide: 106-95-6 / methyl triflate: 333-27-7 / benzaldehyde: 100-52-7 / pivalic aldehyde: 630-19-3 / acrolein: 107-02-8 / acetone: 67-64-1 / chlorotrimethyl silane: 75-77-4