starting material) of **48** as an oily mixture of acetoxy epimers: IR ($CHCl_3$) 3450, 1750, 1670 cm^{-1}; NMR ($CDCl_3$) δ 6.36 (s, 1 H), 5.79 (b s, 1 H), 4.81 (d, 1 H, J = 14 Hz), 4.44 (d, 1 H, J = 14 Hz), 2.98 (s, 1 H), 2.20 (s, 3 H), 1.20 (s, 3 H), 1.17 (s, 3 H), 1.08 (s, 3 H); exact mass 308.164 (calcd for $C_{17}H_{24}O_5$, 308.162).

(5aα,9aβ,9bα)-1,3,5,5a,6,7,8,9,9a,9b-Decahydro-5-oxo-6,6,9a-trimethyl-9b-hydroxy-1,3-dimethoxynaphtho[1,2-*c*]furan (50). A stirred solution of 175 mg (0.57 mmol) of **45** and a catalytic amount of *p*-toluenesulfonic acid in 15 mL of dry methanol was refluxed overnight. The reaction mixture was poured into 25 mL of ether containing 20 mg of anhydrous sodium carbonate and was filtered (Celite). The filtrate was concentrated to a residue which was purified by preparative TLC (12% ethyl acetate/benzene) to yield 129 mg (73%) of **50** as an oily mixture of epimers: IR (neat) 3500, 1670 cm^{-1}; NMR ($CDCl_3$) δ 5.84, 5.77, 5.63, 5.24, 2.14, 4.94 (each a b s, 1 H), 3.35–3.65 (m, 6 H), 3.03, 2.88 (each a b s, 1 H); MS, *m/e* (relative intensity) 279 (7.4, $M^+ - OCH_3$) 250 (100), 235 (43), 217 (37), 181 (49), 167 (56), 140 (48).

6β-Hydroxywarburganal (52). To a stirred solution of 75 mg (0.24 mmol) of **50** in dry THF, cooled in a salt–ice bath, was added 0.6 mL of 1 N DIBAL in *n*-hexane. After 1 h, the mixture was quenched with 25 mL of 10% hydrochloric acid and extracted with ethyl acetate. The organic extract was washed with saturated, aqueous sodium bicarbonate, dried, and concentrated to yield an oil. The NMR spectrum of the crude mixture revealed partial hydrolysis to an aldehyde ($\simeq$10%, δ 9.52 and 9.80) and a mixture of methyl acetals (s between δ 3.3 and 3.7) which were devoid of signals at δ 2.88 and 3.03 present in **50**. The crude product was redissolved in 1.5 mL of acetone and 0.25 mL of 10% hydrochloric acid. After 15 min, the reaction mixture was poured into 25 mL of ethyl acetate and was washed with saturated, aqueous sodium bicarbonate. The organic layer was dried and concentrated to give 73 mg of an oil which crystallized from ether/*n*-hexane to yield 59 mg (92%) of **52** as a colorless solid: mp 154–155 °C; IR (Nujol) 3400, 1710, 1670 cm^{-1}; NMR ($CDCl_3$) δ 9.82 (s, 1 H), 9.53 (s, 1 H), 7.09 (d, 1 H, J = 4.5 Hz), 4.90 (m, 1 H), 1.35 (s, 6 H), 1.12 (s, 3 H); MS, *m/e* (relative intensity) 266 (0.9, M^+), 237 (48), 219 (18), 177 (17), 151 (21), 149 (21), 123 (31), 121 (29), 113 (50), 109 (100); exact mass 266.152 (calcd for $C_{15}H_{22}O_4$, 266.152).

(±)-Cinnamodial (5). To a stirred solution of 10.6 mg (0.039 mmol) of **52** in 0.2 mL of benzene was added 1u μL of triethylamine, 11 μL of acetic anhydride, and a catalytic amount of 4-(dimethylamino)pyridine. After 18 h, 25 mL of ethyl acetate was added. The organic solution was washed with 5% hydrochloric acid and saturated, aqueous sodium bicarbonate and was dried and concentrated to a residue. This was chromatographed (25% ether/*n*-hexane) to yield 10.3 mg (81%) of **5**: mp 127–128 °C (lit.[13] 128–130 °C); IR (Nujol) 3450, 1740, 1720, 1690 cm^{-1}; NMR ($CDCl_3$) δ 9.75 (s, 1 H), 9.46 (s, 1 H), 6.98 (d, 1 H, J = 5 Hz), 5.91 (t, 1 H, J = 5 Hz), 4.10 (b s, 1 H), 2.18 (s, 3 H), 2.09 (d, 1 H, J = 5 Hz), 1.38 (s, 3 H), 1.20 (s, 3 H), 1.06 (s, 3 H); MS, *m/e* (relative intensity) 279 (19, M^+), 148 (13), 237 (33), 343 (27), 219 (22), 109 (29), 105 (21), 69 (28), 55 (26), 43 (100), 41 (35), 29 (16).

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Synthesis and Absolute Configurations of Halogenoallenes

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The highly stereoselective synthesis of 3-methyl-1-halogenoallenes, 3-*tert*-butyl-1-halogenoallenes, and 1,3-di-*tert*-butylallene is described. The *R* absolute configuration is assigned to the levorotatory halogenoallenes by relating them to allenes of known configurations. The configurational assignments are in agreement with (vacuum) circular dichroism data for the *tert*-butylallenes. The obtained results are used to clarify the hitherto existing confusion in the literature concerning absolute configurations of chloro- and bromoallenes. Further, the signs and magnitudes of the ligand specific parameters for the halogens in the chirality functions approach, used to predict optical rotations of allenes, are discussed. The literature parameter for chlorine is revised and adequate numerical values for those of bromine and iodine are proposed.

Recently, a synthetic route to optically active 3-phenyl-1-halogenoallenes **1** and 21-halogeno steroidal allenes **2** of high enantiomeric purity has been described.[2,3] The present investigation demonstrates the utility of the method to obtain optically active 3-alkyl-1-halogenoallenes, viz., 3-*tert*-butyl-1-halogenoallenes **3a–c** and 3-methyl-1-halogenoallenes **4b** and **4c**. These compounds, together with 1,3-di-*tert*-butylallene **3d**, are very interesting from a theoretical point of view, particularly in relation to theoretical treatments of optical rotations of allenes.[4,5] The relatively simple constitution of compounds **3** and **4** (with only rotationally symmetric substituents) renders them extremely useful for spectroscopic investigations such as (vacuum) ultraviolet and circular dichroism spectroscopy. The spectroscopic and chiroptical properties of **3a–d** are discussed elsewhere.[6]

Further, a lot of confusion can be noted in the literature concerning absolute configurations of chloro- and bromoallenes.[4] It has been shown[2] that levorotatory **1a** as well as **1b** possess the *R* configuration. On the other hand, the *S* configuration has been assigned to both levorotatory chloroallene (**5a**) and dextrorotatory bromoallene (**5b**).[7]

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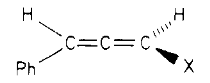
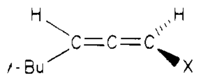


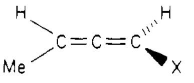
(*R*)-1

1a, X = Cl
b, X = Br
c, X = I



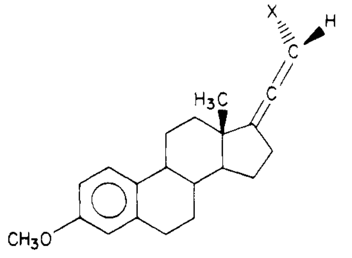
(*R*)-3

3a, X = Cl
b, X = Br
c, X = I
d, X = *t*-Bu

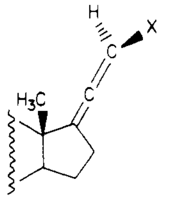


(*R*)-4

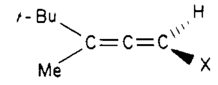
4a, X = Cl
b, X = Br
c, X = I



2a, X = Cl
b, X = Br
c, X = I



2d, X = Cl
e, X = Br



(*S*)-5

5a, X = Cl
b, X = Br

In a theoretical approach to optical rotations of allenes (the "chirality functions approach")[5] which describes molar rotations in terms of ligand specific parameters λ, it has been suggested that the parameter for chlorine, λ (Cl), is negative and that for bromine, λ(Br), is positive. In this work these assignments are reconsidered and adequate numerical values for λ(Cl), λ(Br), and λ(I) are derived.

Synthesis and Absolute Configurations of Allenes 3 and 4. The halogenoallenes **3a–c** could not satisfactorily be synthesized by treatment of propargylic alcohol **6a** with HX/CuX in water.[8] Another method, viz., reaction of alcohol **6a** with thionyl chloride in dioxane, was investigated to prepare the chloroallene **3a**, but in spite of other reports[9] we did not obtain a satisfactory yield of **3a**. Much better results were obtained by using our recently developed method involving halogenocuprate-induced 1,3-substitution of a 2-propynylic methanesulfonate.[2]

Although the methanesulfonate group has proven to be an excellent leaving group in many organocuprate-induced reactions,[2,10] preliminary experiments showed that no reaction of methanesulfonate **6b** with cuprates **8** (see Scheme I) occurred at low (cf. ref 2) or ambient (cf. ref 3) temperature in THF. The use of the more reactive copper(I) species **9** under similar conditions resulted in only a low degree of conversion of **6b** (<10%). However, refluxing **6b** during 2 h with 2.0 (X = Br or I) or 5.0 (X = Cl) mol equiv of cuprates **8** or **9** produced the halogenoallenes **3a–c** in 80–90% yield. The more reactive methanesulfonate **7b** was readily converted into the allenes **4b–c** at 20 °C by using cuprates **8** (1.2 mol equiv, X = Br or I). Contrary to the reported synthesis of **1a–c**,[2] it was not advantageous to use the trihalodicuprates **9** instead of the dihalocuprates **8** since the use of **9** gave rise to formation of considerable amounts (5–20%) of propargylic isomers. By applying **8**, allenes **3a–c** and **4b–c** were contaminated with only minor quantities of their propargylic isomers from which they could easily be purified by column chromatography over alumina containing $AgNO_3$ (see Experimental Section). Unfortunately, chloroallene **4a** was contaminated with 40% of its propargylic isomer and was not further used in our study.

Scheme I

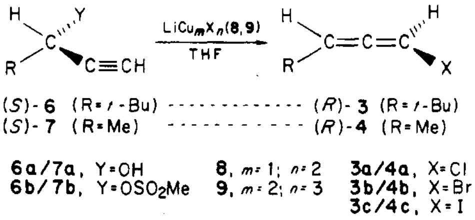


Table I. Optical Rotation Data for Allenes (***R***)-3 and (***R***)-4

no.	X	$[\alpha]^{20}_D$[a]	$[\alpha]^{20}_D$,[b] min	$[\phi]^{20}_D$,[b] min
3a	Cl	-85.5	-225	-294
3b	Br	-87.5	-230	-403
3c	I	-118.0	-314	-697
3d	*t*-Bu	-47.1	-124	-188
4b	Br	-34.5	-157	-208
4c	I	-50.2	-228	-410

[a] In degrees, measured in EtOH; after purification. The values refer to the allenes **3** obtained from 38% ee *t*-BuCH(OH)C≡CH and allenes **4** obtained from 22% ee MeCH(OH)C≡CH, respectively. [b] Extrapolated to 100% ee.

Staring from optically enriched **6b** and **7b**, optically active halogenoallenes were obtained. For our study we used (*S*)-**6b** (38% ee) and (*S*)-**7b** (22% ee).[11] Treatment of these compounds with **8** (or **9**) led to levorotatory **3a–c** and **4b–c**, respectively. Table I gives the specific optical rotations, $[\alpha]_D$, for the purified allenes. In some separate experiments it was established that during the allene formation no racemization of the starting material and products had occurred. It was found, for instance, that refluxing allenes **3a–b** with excess of **8** during 1–2 h in THF did not cause any detectable racemization of **3**. Similarly, **4b** could be stirred with excess of **8** for 2 h at 20 °C without loosing its optical activity. In contrast, diorganocuprates, e.g., Me_2CuLi, are known to induce a rather rapid racemization of alkylallenes.[12] When the conversions of **6b** and **7b** were interrupted and unconverted **6b** and **7b** were hydrolyzed to give **6a** and **7a**, respectively, no loss of enantiomeric purity could be detected for these alcohols, from which **6b** and **7b** had been prepared.

The stereochemical course of the allene formation will be net anti. From previous work it is known that mestranyl methanesulfonate is converted with >99% anti stereoselectivity into steroidal allenes **2**.[3] Also allenes **1a–c** were formed with high anti stereoselectivity.[2] It is therefore quite reasonable to propose the anti substitution mode for the reactions of **6b** and **7b** with **8** (and **9**). In addition, combined (ultraviolet) absorption and CD spectroscopy on allenes **3**[6] corroborate the proposed anti stereochemistry (vide infra). For the time being we assume that, in analogy with the steroid case, the formation of **3**

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(10) See for instance: Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390–392.

(11) (*S*)-**6b** $[\alpha]^{20}_D$ -76.7° (EtOH, *c* 0.8) extrapolated to 100% ee. (*S*)-**6a** $[\alpha]^{20}_D$ -17.2° (neat liquid, *l* = 1 dm) for optically pure **6a**. (*S*)-**7b** $[\alpha]^{20}_D$ -100.0° (EtOH, *c* 1.7) extrapolated to 100% ee. (*S*)-**7a** $[\alpha]^{20}_D$ -52.0° (dioxane, *c* 2.3) for optically pure **7a**.

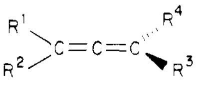
(12) (a) Olsson, L.-I.; Claesson, A. *J. Chem. Soc., Chem. Commun.* **1979**, 679–684. (b) Westmijze, H.; Nap, I. A.; Meijer, J.; Kleijn, H.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 154–157.

and 4 takes place almost stereospecifically. There is no reason to reckon with a direct syn substitution. One could imagine, however, that besides a direct anti 1,3-substitution of **6b** and **7b** a two-step reaction sequence through propargylic halides would be competitive. Such a process would lead to allenes of the opposite configuration if the two reaction steps are anti substitutions. However, this route will not be important as we found, for instance, that the propargylic bromide *t*-BuCH(Br)C≡CH reacts very slowly with $LiCuBr_2$ under the conditions used to convert **6b** into **3b**. In view of what has been said above, we conclude that (*S*)-**6b** and (*S*)-**7b** are converted into *R* halogenoallenes 3 and 4 in a highly stereoselective anti fashion (Scheme I).

For the purpose of comparison, we also prepared 1,3-di-*tert*-butylallene, **3d**. The absolute configuration of this allene, in relation to the sign of its optical rotation at 589 nm, is known.[13] The levorotatory allene **3d** could easily be obtained by reaction of (*S*)-**6b** (38% ee) with 1.1 mol equiv of *t*-BuCu during 3 min at -65 °C in THF. The allene was flash distilled to remove traces of impurities. Table I shows that if we had started from optically pure **6b**, **3d** with an $[\alpha]^{20}_D$ value of -124° (EtOH) would have been obtained. This is the highest value reported thus far for **3d**. As levorotatory **3d** is of *R* configuration,[13] this reaction proceeds anti.

It was already mentioned that the proposed stereochemistry is corroborated by (vacuum) CD spectroscopy. The spectroscopic data are discussed elsewhere.[6] In short, levorotatory **3d** and **3a–c** show strong negative $^1B_2$ and $^1A'$ (π,π^*) CD bands, respectively, which, on the basis of a dynamic coupling model,[14] points to the *R* absolute configuration for (-)-**3a–d**.

Quantitative Aspects of Optical Rotations of Allenes. Recently, a quantitative procedure for the calculations of molar rotations $[\Phi]_D$ (at the wavelength of the sodium D line, $\lambda_D = 589$ nm) of open chain chiral allenes I on the basis of eq 1 has been presented.[5] In eq 1 $\lambda(R^i)$



I

$$\phi_D(R^1,R^2,R^3,R^4) = [\lambda(R^1)-\lambda(R^2)][\lambda(R^3)-\lambda(R^4)] \quad (1)$$

is a ligand specific parameter for the ligand R attached to site *i*. For almost all the ligands considered so far,[4,5] the ligand specific parameters λ(R) are positive. In particular, one has λ(Ph) > λ(*t*-Bu) > λ(Et) > λ(Me) > λ(H), with λ(H) ≡ 0. The above mentioned approach has proven to be a reliable method to deduce absolute configurations and estimate optical rotations of open chain allenes, notably if the allene has only substituents bonded via carbon to the allenic skeleton. The numerics of λ parameters for *heterosubstituents* presented so far[4] are mostly tentative ones.

Concerning the parameters for halogens, there exists some confusion regarding their sign and magnitude.[4,5] The prediction of a negative sign for the λ parameter for chlorine, λ(Cl), and a positive sign for bromine, λ(Br),[4] was based on the experimental configurational assignments to 1-halogeno-4,4-dimethyl-1,2-pentadienes **5** by Landor,[8b] who assigned the *S* configuration to both the levorotatory chloroallene **5a** and the dextrorotatory bromoallene **5b**. However, our work[2,3] and the findings of Dugat et al.[15] point to positive λ parameters for *all* halogens studied. Also, the results presented in this paper are conceivable only when λ(halogen) is positive. Consequently, the sign of λ(Cl) must be revised; it is positive and not negative as proposed earlier.[5] It remains to be seen as to why the chloroallene **5a** points to a negative λ(Cl) value. Work is in progress to elucidate this notorious inconsistency. Referring to the bromoallenes **1b**, **3b**, and **4b**, and iodoallenes **1c**, **3c**, and **4c**, positive values must also be attributed to λ(Br) and λ(I). A positive value for λ(I) is in agreement with the *R* configuration which was proposed for (-)-1-iodo-1,2-octadiene and (-)-1-iodo-3-methyl-1,2-pentadiene.[16]

Table II. Parameters for the Calculation of Molar Rotations of Allenes[a]

X	λ(X)
Cl	+21.5
Br	+29.2
I	+54.0
t-Bu	+13.7[b]

[a] Solvent ethanol; λ(H) ≡ 0. [b] This is also a revised parameter, cf ref 4,5.

Table III. Calculated (eq 1) and Experimental Molar Rotations of Phenylallenes PhCH=C=CHX[a]

no.	X	ϕ_D, deg	$[\phi]^{20}_D$, deg[b]
1a	Cl	+952	+918
1b	Br	+1294	+2408
1c	I	+2392	+3752
1d	*t*-Bu	+607	+638[c]

[a] Of *S* absolute configuration; solvent ethanol. λ(Ph) = +44.3. [b] Experimental values from ref 4,5. [c] Unpublished results, cf. ref 18.

For the quantitative treatment of molar rotations of halogenoallenes, one can start from the λ parameters given in Table II (for the "standard" solvent ethanol[5]). These (average) values[17] are deduced consistently from the rotations of the 3-alkyl-1-halogenoallenes **3** and **4**, using for λ(*t*-Bu) the value $\{[\Phi]_D(\mathbf{3d})\}^{1/2}$ and for λ(Me) the value 7.2.[18] In order to test the significance of the parameters of Table II, the molar rotations of the phenylallenes **1a–d** are calculated. Theoretical (Φ_D) and experimental rotations ($[\Phi]_D$) of **1a–d** with eq 1 and the parameters of Table II and λ(Me) = 7.2 are compared in Table III.

From the data in Table III it is seen that the predictions are quite good for allenes 1 with *t*-Bu and Cl as the substituents (**1d**, **1a**), but that for the bromo- and iodoallene **1b** and **1c** the deviations between Φ_D and $[\Phi]_D$ are large, viz., -46% for **1b** and -36% for **1c**. The success of eq 1 to account for the optical rotations of chloroallenes (rough estimations of λ(Cl) from impure **4a** (vide supra) also point to a value of ≃+22) requires also a revision of the magnitude of the literature value for λ(Cl);[4,5] i.e., λ(Cl) = +21.5. Similarly, the numerics of the parameter λ(Br) are higher than proposed[4,5] and have to be modified according to Table II.

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(13) (a) Bordon, W. T.; Corey, E. J. *Tetrahedron Lett.* **1969**, 313–316. (b) Crabbé, P.; Velarde, E.; Anderson, H. W.; Clark, S. D.; Moore, W. R.; Drake, A. F.; Mason, S. F. *J. Chem. Soc., Chem. Commun.*, 1971, 1261–1264. (c) Moore, W. R.; Anderson, H. W.; Clark, S. D. *J. Am. Chem. Soc.* **1973**, *95*, 835–844. (d) Butler, W. M.; Tanaka, Y.; Koreeda, M. *J. Org. Chem.* **1981**, *46*, 4620–4621.

(14) Mason, S. F. "Optical Rotatory Dispersion and Circular Dichroism"; Cardelli, F., Salvadore, P., Eds.; Heydon: London, 1973; p 35–38.

(15) (a) Dugat, D.; Verny, M. *Bull. Soc. Chim. Fr.* **1971**, 4532–4537. (b) Dugat, D.; Verny, M.; Vessière, R. *Bull. Soc. Chim. Fr.* **1976**, 1903–1908.

(16) Dollat, J.-M.; Luche, J.-L.; Crabbé, P. *J. Chem. Soc., Chem. Commun.* **1977**, 761–762.

(17) The parameters λ(Br), calculated independently from **3b** and **4b**, are equal within 2%, whereas the values for λ(I), derived from **3c** and **4c**, differ only 10%.

(18) Elsevier, C. J. Ph.D. Thesis, State University at Utrecht, 1984.

As the parameters λ(*t*-Bu) and λ(Cl) in Table II are successful for the quantitative treatment of molar rotations of phenyl- and alkylallenes, the deviations observed for the bromo- and iodophenylallene (**1b**, **1c**) in Table III are assumed to be special cases due to the simultaneous presence of the phenyl and bromo or iodo groups, respectively.[19] The parameters λ(X) in Table II are regarded as "true" values. They describe the optical rotations of halogenoallenes correctly when the λ term (eq 1) constitutes the only relevant contribution. In case of **1b** and **1c**, however, eq 1 is not adequate for the appropriate description of the optical rotations. An additional term is necessary to calculate correct rotations of **1b** and **1c**. Work is in progress to substantiate this conjecture.

Experimental Section

General Methods. All reactions were carried out under an inert atmosphere of dry nitrogen. Optical rotations were measured by using a Perkin Elmer 141 polarimeter device with standard cuvettes (l = 1 dm) and absolute ethanol as the solvent; c = 1.5–2.1. IR spectra were recorded on a Perkin Elmer 457 IR spectrometer on films of the neat liquids (NaCl). ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer in CCl_4 and ^{13}C NMR spectra on a Varian CFT-20 spectrometer in $CDCl_3$ with Me_4Si as the internal standard. Preparative GLC was performed on a Hewlett Packard 5750 gas chromatograph, provided with a 2-m 6-mm diameter column containing 10% OV 17 on Chromosorb W-AW-DMCS 80–100 mesh.

Materials. Copper(I) halides were prepared according to the procedure of Keller and Wycoff.[20] Lithium halides were purchased from BDH Chemicals Ltd., Poole, England, and E. Merck, Darmstadt, West Germany, and dried in vacuo at 180 °C. THF (Aldrich) was distilled from $LiAlH_4$ prior to use. Methanesulfonates **6b** and **7b** were prepared from the alcohols by standard procedures.[10] Optically enriched alcohols were obtained according to our method.[18,21] Al_2O_3 (neutral), purchased from Woelm, was treated with 50 mL of a 0.4 M $AgNO_3$ solution per kg of alumina and stored in the dark.

General Procedure. Halogenoallenes 3a–c. To a homogeneous solution of $LuCuX_2$ (20 mmol, X = Br, I; 50 mmol, X = Cl) in dry THF (40 mL, X = Br, I; 85 mL, X = Cl) was added 1.90 g (10 mmol) of methanesulfonate (*S*)-**6b** (38% ee). The mixture was refluxed during 2–2$^{1}/_{2}$ h and then poured into an aqueous NH_4Cl solution containing NaCN (1 g). After extraction with pentane (3 × 50 mL), washing the combined extracts with a dilute aqueous NH_4Cl solution (5 × 200 mL), and drying the extracts over K_2CO_3, the solvent was stripped off in vacuo. The crude halogenoallenes were purified from small amounts of propargylic isomers by column chromatography over alumina (50 g) containing $AgNO_3$ (1 mmol/50 g) with pentane as the eluent. The yield of **3a–c** was 69–80%. Specific rotations of the products are given in Table I. In the case of **3a**, purification by preparative GLC yielded 46% (overall) of >99% pure **3a**, showing a slightly higher specific rotation.

Halogenoallenes 4b–c. To a stirred solution of $LiCuX_2$ (12 mmol) in dry THF (25 mL) was added 1.48 g (10 mmol) of methanesulfonate (*S*)-**7b** (22% ee). The mixture was stirred at 20 °C during 4 h (X = Br) or 3 h (X = I) and then worked up as above. The solvent was stripped off at 0 °C (150 mmHg). The yields (after column chromatography) of **4b** and **4c** amounted to 54% and 84%, respectively. Specific rotations of the products are given in Table I.

1,3-Di-*tert*-butylallene (3d). To a homogeneous solution of *tert*-butylcopper(I) (11 mmol)—prepared in situ by adding, at –65 °C, *t*-BuMgCl (11 mmol) in THF (12 mL) to a solution of CuBr·LiBr (11 mmol) in THF (20 mL) and stirring the mixture for 15 min at –65 °C—methanesulfonate (*S*)-**6b** (38% ee, 10 mmol) was added at –70 °C. After stirring at –65 °C during 3 min the cold reaction mixture was poured into an aqueous NH_4Cl solution containing NaCN (1 g) and worked up as above. The yield of **3d** was 98%.

1-Chloro-4,4-dimethyl-1,2-pentadiene (3a): n^{20}_{D} 1.4605; IR 1957 cm^{-1} (ν C=C=C); mass spectrum, *m/e* 130 for ^{35}Cl ($M^{+}\cdot$); ^{1}H NMR (CCl_4) δ 5.98 (d, 1 H), 5.53 (d, 1 H), 1.10 (s, 9 H), ^{4}J(HC=C=CH) = –5.75 Hz; ^{13}C NMR ($CDCl_3$) δ 199.5 (C-2), 113.1 (C-3), 89.3 (C-1), 32.8 (C-4), 29.5 (C-5).

1-Bromo-4,4-dimethyl-1,2-pentadiene (3b): n^{20}_{D} 1.4865; IR 1952 cm^{-1} (ν C=C=C); mass spectrum, *m/e* 174 for ^{79}Br ($M^{+}\cdot$); ^{1}H NMR (CCl_4) δ 5.90 (d, 1 H), 5.28 (d, 1 H), 1.10 (s, 9 H), ^{4}J(HC=C=CH) = –5.7 Hz; ^{13}C NMR ($CDCl_3$) δ 199.6 (C-2), 112.0 (C-3), 73.0 (C-1), 32.4 (C-4), 29.5 (C-5).

1-Iodo-4,4-dimethyl-1,2-pentadiene (3c): n^{20}_{D} 1.5350; IR 1946 cm^{-1} (ν C=C=C); mass spectrum, *m/e* 222 ($M^{+}\cdot$); ^{1}H NMR (CCl_4) δ 5.68 (d, 1 H), 5.00 (d, 1 H), 1.08 (s, 9 H), ^{4}J(HC=C=CH) = –5.7 Hz; ^{13}C NMR ($CDCl_3$) δ 203.1 (C-2), 107.4 (C-3), 36.4 (C-1), 31.7 (C-4), 29.6 (C-5).

2,2,6,6-Tetramethyl-3,4-heptadiene (3d): bp 52 °C (18 mmHg); n^{20}_{D} 1.4375; IR 1958 cm^{-1} (ν C=C=C); mass spectrum, *m/e* 152 ($M^{+}\cdot$); ^{1}H NMR (CCl_4) δ 5.09 (s, 2 H), 1.00 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 198.1 (C-4), 104.6 (C-3 + C-5), 31.5 (C-2 + C-6), 30.1 (C-1 + C-7).

1-Bromo-1,2-butadiene (4b): n^{20}_{D} 1.5240; IR 1952 cm^{-1} (ν C=C=C); mass spectrum, *m/e* 132 for ^{79}Br ($M^{+}\cdot$); ^{1}H NMR (CCl_4) δ 5.85 (dq, 1 H), 5.29 (dq, 1 H), 1.82 (dd, 3 H), $^{3}J(H_3CCH)$ = 7.2 Hz, ^{4}J(HC=C=CH) = –5.7 Hz, $^{5}J(H_3CC{=}C{=}CH)$ = 2.5 Hz; ^{13}C NMR ($CDCl_3$) δ 202.8 (C-2), 95.6 (C-3), 71.3 (C-1), 13.8 (C-4).

1-Iodo-1,2-butadiene (4c): n^{20}_{D} 1.5880; IR 1944 cm^{-1} (ν C=C=C); mass spectrum, *m/e* 180 ($M^{+}\cdot$); ^{1}H NMR (CCl_4) δ 5.61 (dq, 1 H), 5.01 (dq, 1 H), 1.80 (dd, 3 H), $^{3}J(H_3CCH)$ = 7.2 Hz, ^{4}J(HC=C=CH) = –5.7 Hz, $^{5}J(H_3CC{=}C{=}CH)$ = 2.7 Hz; ^{13}C NMR ($CDCl_3$) δ 206.0 (C-2), 91.0 (C-3), 34.7 (C-1), 13.1 (C-4).

Registry No. **1a**, 81158-17-0; **1b**, 81158-18-1; **1c**, 81158-19-2; **1d**, 94137-70-9; **3a**, 94137-71-0; **3b**, 94137-72-1; **3c**, 94137-73-2; **3d**, 22688-41-1; **4a**, 94137-74-3; **4a** propargylic isomer, 3355-17-7; **4b**, 94137-75-4; **4c**, 94137-76-5; **6a**, 90865-49-9; **6b**, 94137-77-6; **7a**, 2914-69-4; **7b**, 73647-37-7; **8** (X = Cl), 38363-83-6; **8** (X = Br), 78722-68-6; **8** (X = I), 81314-32-1; **9** (X = Cl), 79950-16-6; **9** (X = Br), 79950-13-3; **9** (X = I), 94137-78-7; *tert*-butylcopper(I), 56583-96-1.

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[19] We do not have reasons to assume different stereoselectivities for the formation of allenes **3** and **4** on the one hand and that of allenes **1** and **2** on the other.

[20] Keller, R. N.; Wycoff, H. D. "Inorganic Synthesis", 1st ed.; McGraw-Hill: New York, 1946; Vol. II, p 1.

[21] Tadema, G.; Wijkens, P.; Elsevier, C. J.; Vermeer, P., unpublished results.