Compound 15 (white solid, mp 53–54 °C): NMR ($CDCl_3$) δ 6.93 (1 H, m), 4.80 (2 H, m), 4.40 (2 H, t, J = 6 Hz), 2.3–2.7 (2 H, cm), 2.15 (3 H, s); IR ($CHCl_3$) 1740, 1720, 1650 cm^{-1}; mass spectrum, m/z 170 (M^+), 128, 127, 110, 82.

Compound 16 (white solid, mp 41–42 °C): NMR ($CDCl_3$) δ 7.58 (1 H, s), 4.68 (2 H, s), 4.52 (2 H, t, J = 6 Hz), 2.65 (2 H, t, J = 6 Hz), 2.02 (3 H, s); IR (CCl_4) 1730, 1675, 1620 cm^{-1}; mass spectrum, m/z 170 (M^+), 127, 111, 83, 43.

Compound 17 (oil bp 118–119 °C at 0.1 mbar): NMR (CCl_4) δ 6.70 (1 H, m), 4.52 (2 H, s), 4.27 (2 H, t, J = 6 Hz), 4.10 (2 H, m), 3.25 (3 H, s), 2.2–2.7 (2 H, cm); IR (CCl_4) 1730, 1625 cm^{-1}; mass spectrum, m/z 141 (M^+ – 31), 127, 112, 45.

Compound 18 (oil, bp 97–98 °C at 0.05 mbar): NMR (CCl_4) δ 7.20 (1 H, s), 4.47 (2 H, s), 4.40 (2 H, t, J = 6 Hz), 4.0 (2 H, s), 3.26 (3 H, s), 2.5 (2 H, t, J = 6 Hz); IR (CCl_4) 1730, 1685, 1625 cm^{-1}; mass spectrum, m/z 141 (M^+ – 31), 127, 112, 83, 45.

Registry No. 1, 3174-74-1; 2, 16302-35-5; 3, 29687-18-1; 4, 88981-46-8; 5, 88981-47-9; 6, 493-05-0; 7, 88981-48-0; 8, 88981-49-1; 9, 3393-45-1; 10, 2381-87-5; 11, 72649-02-6; 12, 85287-76-9; 13, 88981-50-4; 14, 4702-34-5; 15, 88981-51-5; 16, 88981-52-6; 17, 88981-53-7; 18, 88981-54-8; PCC, 26299-14-9; 3-ethyl-4-chlorotetrahydropyran, 35952-04-6.

Stereochemistry of the $HCuX_2$-Induced Formation of 1-Halo-3-phenylpropadienes from 1-Phenyl-2-propyn-1-ol and Some of Its Derivatives

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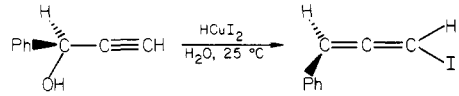
The lithium and tetrabutylammonium dihalocuprate induced conversions of 2-propynylic methanesulfonates,[1,2] methanesulfinates,[2] and chlorides[3] into 1-haloallenes proceed with high anti stereoselectivity. On the other hand, syn stereoselectivity has been observed for the $HCuBr_2$-induced conversion of a propargylic alcohol into the corresponding 1-bromoallene.[4] In this context it was of interest to know whether the syn stereoselectivity is a general feature of the $HCuX_2$-mediated 1-haloallene formation. It will be shown in this paper that this is not the case.

For our study we used (*R*)-(–)-1-phenyl-2-propyn-1-ol (**1a**), a compound that is readily available in optically pure form.[5] Treatment of optically pure (*R*)-(–)-**1a** with 1.0 equiv of $HCuI_2$—prepared by mixing equimolar amounts of CuI and HI with water as solvent—produced, after a 5 min reaction time at 25 °C, nearly quantitatively the 1-iodoallene **2a** (eq 1). The allene was dextrorotatory



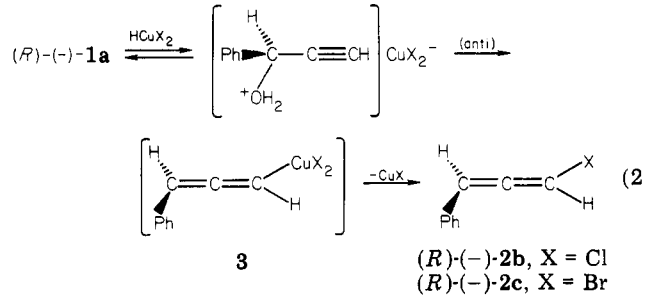
(1)

(*R*)-(–)-**1a** (*S*)-(+)-**2a**

([α]$^{20}_D$ (in EtOH) +90°), which corresponds to the *S* configuration (cf. ref 1); i.e., the formation of **2a** had occurred with syn stereoselectivity, albeit that (*S*)-**2a** was obtained in a very small enantiomeric excess (ee ≃ 6%).[6] The result appeared to be reproducible.

Quite remarkably, anti stereoselectivity was observed when **1a** was allowed to react with $HCuCl_2$ and $HCuBr_2$ (see also eq 2). Thus, treatment of optically pure (*R*)-(–)-**1a** with $HCuX_2$ (X = Cl or Br) during 5 min at 25 °C gave reproducibly and in high chemical yield (≥95%) the levorotatory allenes PhCH=C=CHX (**2b**, X = Cl, [α]$^{20}_D$ (in EtOH) –25°; **2c**, X = Br, [α]$^{20}_D$ (in EtOH) –280°). The negative value for [α]$_D$ in these cases corresponds with a preferent formation of the (*R*)-allenes (cf. ref 1). In the case of **2b** the optical yield is very low (ee ≃ 4%),[6,7] but for **2c** it is much better (ee ≃ 22%).[6] The stereoselectivity for the formation of (*R*)-**2b** from (*R*)-**1a** could be slightly improved (ee ≃ 8%) by using 0.5 equiv of $HCuCl_2$. When cuprates were used that had been prepared from CuX and excess of HX (cf ref 4), the enantiomeric purity of the allenes **2** decreased considerably. An excess of HX was therefore avoided during our experiments.[8]

Landor et al. reported that the amount of syn stereoselectivity in their case, viz., conversion of 3,4,4-trimethyl-1-pentyn-3-ol by $HCuBr_2$, was high.[4] The authors proposed a mechanism involving the rapid formation of a π-complex between the carbon–carbon triple bond of the alcohol and the cuprate $CuBr_2^-$ followed by a rate-determining S_Ni'-type reaction (cf ref 4). Such a mechanism could be valid for the reaction of **1a** with $HCuI_2$, but the low optical yield for this conversion indicates that other processes, e.g., formation of **2a** through the cation Ph^+-CHC≡CH leading to racemic **2a** and/or the occurrence of synchronous anti 1,3-substitution, must be important. It is even possible that the overall syn stereoselectivity is caused by a preferent occurrence of a reaction sequence involving two successive anti substitutions, viz., (i) conversion of (*R*)-**1a** into (*S*)-PhCH(I)C≡CH and (ii) conversion of this propargylic iodide into (*S*)-**2a**. We do not have evidence to exclude the latter route. The anti stereoselectivity for the $HCuCl_2$- and $HCuBr_2$-induced conversions of **1a** is similar to that reported in ref 1–3. Equation 2 presents a mechanistic proposal for these re-



(2)

3 (*R*)-(–)-**2b**, X = Cl; (*R*)-(–)-**2c**, X = Br

actions involving the initial protonation of the hydroxyl group of **1a** in order to improve its leaving group character, followed by the formation of the copper(III) intermediate **3**[9] in an anti 1,3-substitution reaction; reductive elimination

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(5) Tadema, G.; Everhardus, R. H.; Westmijze, H.; Vermeer, P. *Tetrahedron Lett.* **1978**, 3935.
(6) The ee values are calculated assuming that the [α]$^{20}_D$ values that are given in ref 1 for the haloallenes **2** refer to optically pure compounds.
(7) The allene was contaminated with 5 mol % of PhCH(Cl)C≡CH.
(8) Alcohol **1a** can also be converted into allenes **2** by using only HX (water as solvent). For instance, reaction of **1a** with 2.0 equiv of HI (for concentration of HI, see under Materials) gave after 5 min a quantitative yield of allene **2a**; after shorter reaction periods, mixtures of **2a** and **1a** were obtained. When HCl or HBr instead of HI was used, the main product was initially the propargylic halide PhCH(X)C≡CH, which, under the conditions of the reaction, isomerized almost completely (≥98%) into the allenic halide PhCH=C=CHX (**2b**, X = Cl; **2c**, X = Br) by excess of HX. Such an initial formation of the propargylic halide has not been observed during the $HCuX_2$-promoted reactions of **1a**.

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of **2** from **3** is assumed to proceed with retention of configuration in the allenyl unit.[10]

Also here other conversion modes of **1a** into **2b** and **2c** than the one outlined in eq 2 must be important in view of the low ee values, especially for X = Cl. Such competing processes could be, for instance, the occurrence of syn 1,3-substitution (vide supra) and/or the initial formation of the cation $Ph^+CHC{\equiv}CH$. A rapid racemization of **1a** by $HCuX_2$ prior to its conversion into **2** is not likely as we found that, after treatment of **1a** with less than 1.0 equiv of $HCuX_2$ (studied for X = Cl, Br) followed by recovering and analysis of unconverted **1a**, no detectable racemization of **1a** had taken place. In some separate experiments the methyl ether of **1a**, (*R*)-PhCH(OMe)C≡CH (**1b**),[11] and the sulfinate ester of **1a** (R_c)-PhCH(OS(O)Me)C≡CH (**1c**)[11] were reacted with $HCuX_2$. Ether **1b** reacted much slower with $HCuX_2$ than alcohol **1a**. When X in the cuprate was I, no satisfactory conversion could be realized. When X was Cl or Br, the allenes **2b** and **2c** were obtained in excellent yield (≥95%) by reaction of **1b** with 2.0 equiv of $HCuX_2$ during 30 min at 25 °C. Within experimental error the enantiomeric purities of the formed levorotatory allenes **2b** and **2c** were identical with those found starting from **1a**. However, the reaction of optically pure sulfinate (R_c)-**1c** with $HCuCl_2$ and $HCuBr_2$ proceeded with better anti stereoselectivity. Thus, treatment of **1c** at 25 °C with 1.0 equiv of $HCuCl_2$ during 2 min or with 1.0 equiv of $HCuBr_2$ during 0.5 min, quantitatively produced levorotatory **2b** and **2c** showing $[\alpha]^{20}_D$ values (in EtOH) of −150° and −630°, respectively. These specific rotations correspond to ee values of 24% for (*R*)-**2b** and 52% for (*R*)-**2c**.[6] From other work it is known that the sulfinate group is an excellent leaving group in organocopper(I) reactions.[10b,c] The increased stereoselectivity obtained by using this group is undoubtedly due to an increased contribution of the reaction mode of eq 2 to the substitution process (replace the OH function in eq 2 by OS(O)Me). Interestingly, also the reaction of (R_c)-**1c** with $HCuI_2$ showed anti stereoselectivity, albeit to a small extent (ee ≃ 6%).[6]

To summarize, the presented study shows that syn stereoselectivity is not a general feature for the 1-haloallene formation from propargylic alcohols by using the Landor reagent. Comparison of Landor's data with those presented here indicates that the nature of the substituents at the propargylic center of the starting alcohol may importantly influence the stereochemical course of the allene formation. The study further shows that the Landor reagent can also be used to substitute groups other than hydroxyl, in the case of the sulfinate group even with a better stereochemical result.

Experimental Section

General Procedures. All reactions were carried out in an inert atmosphere of dry nitrogen. Optical rotations were measured in a Perkin-Elmer Model 241 polarimeter by using standard cuvettes (1 = 10 cm) at 20 °C.

Materials. Aqueous solutions of hydrochloric acid (37%, w/w), hydrobromic acid (47% w/w), and hydroiodic acid (57%, w/w) were purchased from Merck-Darmstadt. Hydroiodic acid was distilled prior to use. The copper(I) halides were obtained according to the method of Keller and Wycoff.[12] Optically pure (*R*)-(−)-PhCH(OH)C≡CH (**1a**; $[\alpha]^{25}_D$ 20.8°, in dioxane) was prepared according to our procedure.[5] Optically enriched (*R*)-(−)-PhCH(OMe)C≡CH (**1b**; $[\alpha]^{20}_D$ −29.0°, in EtOH; ee 50%) was obtained by adding, at −60 to −50 °C, 13.5 mL of *n*-butyllithium (1.50 M) in hexane to a stirred solution of 2.64 g of **1a** (20.0 mmol, ee 50%) in 60 mL of dry THF. After 5 min, 10 mL of dimethyl sulfoxide and 5.8 g of methyl iodide (58.0 mmol) were successively added. The mixture was stirred during 1.0 h at 25 °C and then poured into 200 mL of an aqueous NH_4Cl solution. The product was extracted with pentane/ether (80/20 v/v, 2 × 100 mL). The combined extracts were washed with a dilute NH_4Cl solution (5 × 300 mL), dried with K_2CO_3, and concentrated in vacuo, yielding colorless **1b** in 94% yield and in high purity (>98% by GLC). The methanesulfinate (R_c)-(−)-PhCH(OS(O)Me)C≡CH (**1c**; $[\alpha]^{20}_D$ −15.8°, in EtOH, ee 25%)[13] was prepared from (*R*)-**1a** (ee 25%) and methanesulfinyl chloride by using triethylamine as a base.[10b]

General Procedure for the Conversion of 1a–c into Allenic Halides 2a–c. Compounds **1a–c** (3.0 mmol) were added, at 25 °C, to a solution of $HCuX_2$ (3.0 or 6.0 mmol, see text) in water. After shaking the resulting mixture during 0.5–30 min (see text), the products were isolated by extraction with pentane (4 × 10 mL). The combined extracts were washed once with 10 mL of concentrated HX (see under Materials paragraph) in order to remove CuX and then with a dilute aqueous K_2CO_3 solution in order to remove all acid. The extracts were dried with K_2CO_3; and the solvent was evaporated in vacuo. The obtained allenes proved to be identical with those already described in ref. 1. The $[\alpha]_D$ values were determined immediately (X = I; column chromatography caused some racemization) or after column chromatography (X = Cl or Br; Al_2O_3 + 5% H_2O, elution with pentane). In the latter cases only a slight increase of the rotations was observed by the chromatographic purification. The required cuprates $HCuX_2$ were obtained by shaking, at 25 °C, CuX (3.0 or 6.0 mmol) during 2 min with an equimolar amount of HX in water (for concentrations of HX, see under Materials paragraph).

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Registry No. (*R*)-(−)-**1a**, 61317-73-5; (*R*)-(−)-**1b**, 89178-57-4; (*R*)-(−)-**1c**, 70000-50-9; (*S*)-(+)-**2a**, 81158-19-2; (*R*)-(−)-**2b**, 68276-38-0; (*R*)-(−)-**2c**, 89178-58-5; $HCuCl_2$, 18460-62-3; $HCuBr_2$, 43403-59-4; $HCuI_2$, 87890-94-6; CuI, 7681-65-4; HI, 10034-85-2; HCl, 7647-01-0; HBr, 10035-10-6; CuCl, 7758-89-6; CuBr, 7787-70-4.

(9) The copper(III) concept is frequently used to explain organocopper(I)-induced cross-coupling reactions, but its validity is still a matter of discussion. It has been critized, for instance, by: Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. These authors believe that Cu(II) rather than Cu(III) species are involved.

(10) See, for related mechanistic proposals, for instance: (a) Luche, J. L.; Barreiro, E.; Dollat, J. M.; Crabbé, P. *Tetrahedron Lett.* **1975**, 4615. (b) Vermeer, P.; Westmijze, H.; Kleijn, H.; Van Dijck, L. A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 56. (c) Oostveen, E. A.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Ibid.* **1982**, *101*, 382.

(11) In practice no optical pure **1b** and **1c** were used. Compound **1b** mainly consisted of the *R* enantiomer (ee 50%); for compound **1c** the ee value for the R_c compound amounted to 25%. The indicated $[\alpha]_D$ values for **2b** and **2c** obtained from these substrates are extrapolated values and refer to optically pure substrates.

(12) Keller, R. N.; Wycoff, H. D. In "Inorganic Syntheses", 1st ed.; McGraw-Hill: New York, London, 1946; Vol. II.

(13) Hydrolysis of the ester showed that no loss of enantiomeric purity had occurred during its preparation.

Hydrogen Abstraction Selectivities for Ground-State, S_π, and Excited-State, S_σ, Succinimidyl Radicals: Cyclopentane/Cyclohexane. Origins and Resolution of Disputed Data[1]

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Three distinctive hydrogen abstractors have been recognized[2-10] in systems containing Br_2 and NBS: Br, S_π,

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