organic molecule by thermal methods and render the material microporous have not been successful, and we are now pursuing softer chemical techniques (such as Soxhlate extraction). Preliminary results indicate that related structures are formed under hydrothermal conditions with other structure-directing agents.

Experimental Section

The title compound was synthesized from a tin phosphate gel containing en as a structure-directing agent. Tin(II) oxalate (Aldrich), phosphoric acid (85 wt%, Aldrich), en (Aldrich), and water in a ratio of 1.0:1.0:1.0:55 were mixed and stirred until homogeneous. The mixture was sealed in a PTFE-lined, stainless-steel autoclave (Parr, USA) and heated at 160 °C for 2 days under autogeneous pressure. The resulting product, containing predominantly colorless single crystals, was filtered and washed thoroughly with deionized water. A suitable, needle-like single crystal ($0.025 \times 0.025 \times 0.15$ mm) was selected under a polarizing microscope. The crystal structure determination was performed on an Enraf-Nonius CAD4-MACH four-circle diffractometer equipped with a Rigaku rotating anode (Cu_{K_α} radiation, $\lambda = 1.5418$ Å). The unit-cell constants were determined from 25 well-centered reflections within $43.0 \leq 2\theta \leq 60.8°$. Crystal data for *en*-SnPO-1: orthorhombic, space group *Pnaa* (no. 56 non-standard setting), $a = 9.7876(7)$, $b = 15.0686(10)$, $c = 20.8523(19)$ Å, $V = 3078.18(1)$ Å^3, $Z = 8$, $M_r = 790.73(1)$ and $\rho_{calcd} = 3.412(1)$. Data were collected at 25 °C with ω-2θ scans and scan width $\Delta\omega = (1.0 + 0.15 \tan\theta)°$ extending 25% on each side for background measurement. A total of 3799 reflections were collected at $1 \leq 2\theta \leq 144°$ and merged to give 2819 unique data ($R_{merg} = 3.75$), of which 2304 with $I > 3\sigma(I)$ were considered to be observed. The structure was solved by direct methods with SHELXS-86 [24] and difference Fourier syntheses. Final $R = 3.98$, $R_w = 4.56$, and $S = 1.4$ were obtained for 211 parameters. Absorption correction was carried out with the DIFABS calculation routine. DIFABS minimum and maximum correction: 0.78 and 1.83. Hydrogen atoms on the amine groups were placed geometrically and held in the riding mode. Final Fourier map minimum and maximum: -1.39 and $1.70\ e\text{Å}^{-3}$. Full-matrix, least-squares structure refinement against $|F|$ was carried out with the CRYSTALS [25] program package. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344, Eggenstein-Leopoldshagen (Germany), on quoting the depository number CSD-405960.

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A Highly Stereoselective Synthesis of β-Trifluoromethylated Homoallylic Alcohols in Water**

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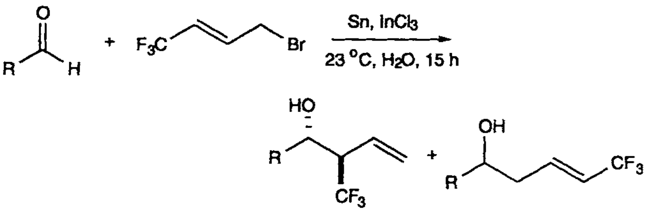
Growing interest in trifluoromethylated organic compounds in fields such as medicine, pharmaceuticals, and fluoropolymers has led to a new focus on discovering a facile method for introducing trifluoromethyl groups into useful intermediates or desired substrates.[1] The trifluoromethyl group—with its strong electronegativity, stability, and lipophilicity—often induces considerable changes in chemical, physical, and physiological properties upon the transformed molecule. However, synthetic methods for introducing this group into a special site of organic compounds suffered from low reactivity and selectivity.[2] Consequently, the synthesis of intermediates carrying a trifluoromethyl group is an attractive approach. In connection with our interest in developing a practical method for trifluoromethylation in aqueous solution, we found that β-trifluoromethylated homoallylic alcohols can be easily synthesized by allylation in water. The novel reagent 1,1,1-trifluoro-4-bromobut-2-ene reacted with various aldehydes in the presence of tin and $InCl_3$ to form trifluoromethylated allylated products in high yields and excellent regio- and diastereoselectivities (Scheme 1).



Scheme 1. Synthesis of β-trifluoromethylated homoallylic alcohols in water.

1,1,1-Trifluoro-4-bromobut-2-ene was prepared by reduction of commercially available 4,4,4-trifluorocrotonate (Scheme 2) and bromination of the resulting alcohol with PBr_3. The

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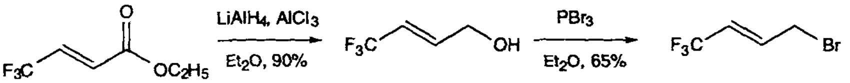
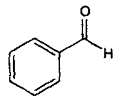
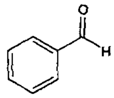
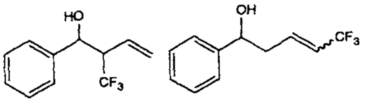
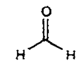
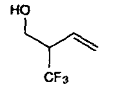
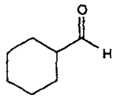
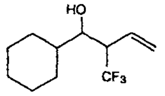
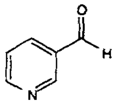
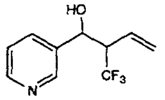
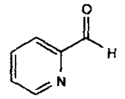
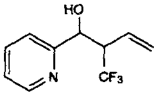
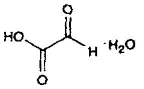
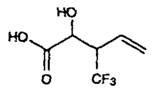


Scheme 2. Synthesis of 1,1,1-trifluoro-4-bromobut-2-ene from 4,4,4-trifluorocrotonate.

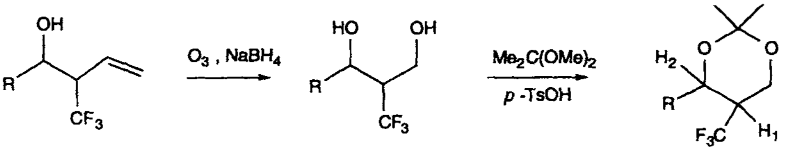
product was purified by fractional distillation of the ether extract. The allylation reactions of aldehydes and this trifluoromethylated allylic bromide were performed under optimized conditions,[3] and reactions proceeded very smoothly at room temperature. The results are shown in Table 1.

We discovered that, unlike in our previous work,[3a] $InCl_3$ is essential for tin-mediated allylation (entries 1 and 2). High yields of the coupling products were obtained in all cases, and several characteristic features were observed. 1) This reaction used in this reaction directly (entries 3 and 7). 3) The γ-coupled product was the major one for the described conditions, and the regioselectivity was dependent on the type of aldehyde used. 4) The diastereoselectivity of the reaction was excellent. The *anti* products were the major isomers in most allylation reactions. 5) The *syn* product formed only when 2-pyridinecarboxaldehyde and glyoxylic acid were used.

Table 1. Allylation reaction of aldehydes with 1,1,1-trifluoro-4-bromobut-2-ene [a].

Entry	Aldehyde	Product	Yield (%) [b] (*anti*:*syn*) [c]
1		–	0 [d]
2		 γ coupling (γ:α 91:9) α coupling (*E*:*Z* 60:40)	87 (95:5)
3			90
4			92 (100:0)
5			95 (92:8)
6			96 (0:100)
7			83 (0:100)

[a] All reactions were carried out on a 0.5–1 mmol scale, see Experimental Section. [b] Yield of purified product. The α, γ, and *syn*, *anti* isomers were separated by column chromatography on silica gel. [c] Determined by ^1H and ^{19}F NMR. [d] No $InCl_3$ was added in this reaction.



1a R=Ph
1b R=2-pyridine

2

3a $J_{\text{H1-H2}}$ = 10.11 Hz
3b $J_{\text{H1-H2}}$ = 1.43 Hz

Scheme 3. Determination of the configuration of **1** by chemical manipulation to the corresponding acetonide **3**.

The configuration of the allylation product was confirmed by chemical manipulation to the corresponding acetonide **3** (Scheme 3). Compound **1** was ozonolyzed and then directly reduced to diol **2**,[4] which was allowed to react with 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-TsOH to furnish **3**. The *anti* and *syn* stereochemistry of **1a** and **1b**, respectively, was deduced from the ^1H NMR coupling constant of the axial proton adjacent to both the hydroxy and trifluoromethyl group in **3a** and **3b**.

No allylation occurred in the absence of $InCl_3$, indicating its significance in the transmetalation process.[3a] Interestingly, some α-coupling adduct was produced along with the γ product. Based on the transmetalation mechanism, the α product would form when reactive aldehyde attacked the allyl indium species **4** (Scheme 4). The strong preference for reaction of the *anti* adduct can be explained by the six-membered transition state. The trifluoromethyl group is in an equatorial position and appears to be sterically very bulky. This is consistent with the findings of Corey et al. as well as Kitazume and Yamazaki et al.[5] In contrast, the high *syn* selectivity observed with 2-pyridinecarboxaldehyde and glyoxylic acid indicates that the 2-pyridinyl and COOH groups prefer the axial position. This is probably due to the five-membered ring chelation with indium shown in Scheme 4.

This study provides a highly stereoselective method for synthesizing β-trifluoromethylated homoallylic alcohols, which may be readily transformed into biologically active compounds. Further investigations are in progress for applying this methodology to the synthesis of optically pure trifluoromethyl compounds.

Experimental Section

General procedure for the synthesis of β-trifluoromethylated homoallylic alcohols: The aldehyde (1 mmol) was added to a mixture of tin powder (1.5 mmol), $InCl_3$ (1.5 mmol), and 1,1,1-trifluoro-4-bromobut-2-ene (1.5 mmol) in H_2O (5 mL). The resulting suspension was stirred at room temperature for 15 h. After usual workup, the product was purified by chromatography on silica gel.

1-(3-Pyridinyl)-2-trifluoromethylbut-3-en-1-ol (colorless oil): ^1H NMR ($CDCl_3$): δ(major product) = 2.90–2.94 (m, 1H), 5.07 (d, 1H, J = 17.24 Hz), 5.24(d, 1H, J = 3.23 Hz), 5.37 (d, 1H, J = 10.38 Hz), 5.89–5.96(m, 1H), 7.28 (m, 1H), 7.70 (m, 1H), 8.45 (m, 2H); δ(minor product) = 5.45 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 148.79, 147.56, 137.22 134.48, 127.02, 126.29, 124.78, 124.26, 123.31, 68.80; ^{19}F NMR ($CDCl_3$): δ = 8.05 (d, CF_3, J = 7.32 Hz); EI-HRMS calcd for $C_{10}H_{10}F_3NO$: 217.07144, found: 217.07261.

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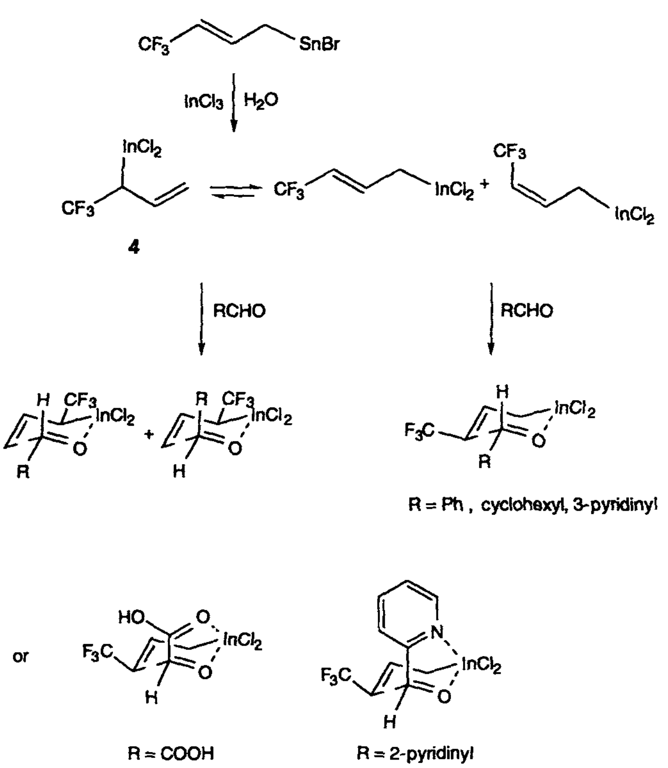

Scheme 4. Mechanism of the transmetalation via a six-membered transition state.

Keywords: aldehydes · allylation · fluorine · indium · tin

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[4] During structure determination it was found that decomposition of ozonide from **1** with methyl sulfide gave a complicated mixture of products.

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$(CuI)_3Cu_2TeS_3$: Layers of Cu_2TeS_3 in Copper(I) Iodide**

Arno Pfitzner* and Stefan Zimmerer

The reactivity of copper(I) halides toward the chalcogens S, Se, and Te is completely different from that of the corresponding silver and gold halides. Thus, up to now for copper halides only compounds containing *neutral* chalcogen fragments, such as screwlike $^1_\infty[Te^0]$ and $^1_\infty[Se^0]$ chains or six-membered Se rings, are known. They can be described as adducts of copper(I) halides and neutral polymeric or oligomeric chalcogen ligands. Typical compositions are CuClTe, $CuClSe_2$, and $CuISe_3$.[1-3] With the exception of AgITe,[4] which also contains neutral Te chains, the corresponding compounds of silver and gold have to be described as mixed chalcogenide halides, that is the chalcogen atoms are *negatively* charged in these compounds. Examples are known containing either divalent anions (Ag_5Te_2Cl[5]) or dianions ($AuTe_2Cl$[6]). In systematic investigations on new adducts of copper halides with neutral polymeric ligands, we recently synthesized ordered mixed-chalcogen chains $^1_\infty[SeTe^0]$ in CuXSeTe (X = Cl, Br, I)[7] and $^1_\infty[STe^0]$ in CuXSTe (X = Cl, Br).[8] In $CuISe_{1.5}Te_{1.5}$ we obtained the hitherto unknown six-membered Se_3Te_3 rings.[9] Compounds of copper(I) halides with phosphorus contain either neutral polymers, for example $^1_\infty[P^0_{12}]$ in $(CuI)_3P_{12}$[10] and $^1_\infty[P^0_{14}]$ in $(CuI)_2P_{14}$,[11] or polyanions, for example $^1_\infty[P^{1-}_{15}]$ in $Cu_3P_{15}I_2$[12] or $^1_\infty[P^{2-}_{20}]$ in $Cu_{12}P_{20}Br_{10}$.[13] Evidently, the copper halide matrix is very flexible and adapts to numerous different ligands.

In an attempt to synthesize the "missing" compound CuISTe, we obtained the first example of a complex chalcogenide ion in the copper(I) halide matrix. Here we report on the synthesis, crystal structure, and spectroscopic investigations of $(CuI)_3Cu_2TeS_3$. This compound crystallizes as large black shiny hexagonal plates and its crystal structure was determined by single-crystal X-ray diffraction.[14] It contains layers of the complex thioanion $[TeS_3]^{2-}$ embedded between layers of iodide ions (Figure 1 left). Thiotellurate(IV) ions have been observed in a limited number of solids, such as $RbCuTeS_3$,[15] $BaTeS_3$,[16] and $(NH_4)_2TeS_3$,[17] and are rarely observed in minerals.[18] In $(CuI)_3Cu_2TeS_3$ all $[TeS_3]^{2-}$ units within one layer are oriented parallel, that is the central tellurium atoms are directed towards one layer of iodide ions and the corresponding sulfur atoms towards another iodide layer. As a consequence the tellurium atoms in the title compound have no additional sulfur atoms as next nearest neighbors but can be regarded as isolated in the copper halide matrix. Nevertheless, no drastic effect on the interatomic distances compared to those in the above-mentioned solids is observed for the $[TeS_3]^{2-}$ group in $(CuI)_3Cu_2TeS_3$ (Figure 2). With an average value of $\bar{d}$(Te–S) = 2.374 Å they fit well with the published data and are about 0.11 Å smaller than the $\bar{d}$(Te–S) distance of 2.48 Å in *neutral* $^1_\infty[STe^0]$ chains.[8] By contrast the average S-Te-S bond angle is 96.35° and is thus about 5° smaller than those in the other examples for thiotellurate(IV) ions and in the *neutral* $^1_\infty[STe^0]$ chains. FT-IR spectroscopy reveals two vibrational frequencies for the $[TeS_3]^{2-}$ group, a strong band at 330 cm^{-1} and a weak one at 374 cm^{-1}. Since the

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