Regio- and Stereoselective Preparation of 3-Trimethylsilylallylic Alcohols by Solvolysis of 2-Trimethylsilylic Derivatives of 1-Bromo- and 1,1-Dibromocyclopropanes in the Presence of $CuSO_4$

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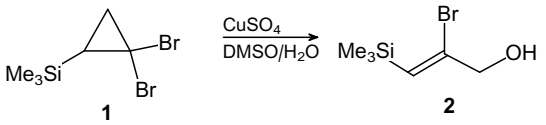
The interaction of 1-bromo- and 1,1-dibromocyclopropanes with an equimolar quantity of $CuSO_4$ in a DMSO–water mixture (molar ratio halocyclopropane:$CuSO_4{\cdot}5H_2O$:DMSO:H_2O = 1:1:10–12:14–16) proceeds *via* cleavage of the three-membered ring to selectively give the most thermodynamically stable isomers of the corresponding 3-trimethylsilyl-substituted allylic or 2-bromoallylic alcohols.

The solvolysis reactions of 1-halo- and 1,1-dihalo-substituted alkyl- and arylcyclopropanes[1–9] are accompanied by opening of the cyclopropane ring (CPR) and are most frequently carried out in the presence of Ag or Cu salts to give *E,Z*-isomer mixtures of the corresponding allylic or haloallylic alcohols.

In the present work we have investigated for the first time the solvolysis of 2-trimethylsilylic derivatives of 1-bromo- and 1,1-dibromocyclopropanes, under previously determined conditions,[1] in the presence of copper and its salts in aqueous DMSO at 112–117 °C. It was shown that, in comparison with alkylcyclopropanes,[1] CPR scission in these cases occurs stereoselectively with the formation of only one of the most thermodynamically stable isomers of allylic alcohols.

The experiments were conducted with a molar ratio halocyclopropane:$CuSO_4{\cdot}5H_2O$:DMSO:H_2O equal to 1:1:10–12:14–16. (*Z*)-1-Trimethylsilyl-2-bromoprop-2-en-3-ol **2** (yield 64%) is selectively formed from 1-trimethylsilyl-2,2-dibromocyclopropane **1** (112–117 °C, 2.5 h).†

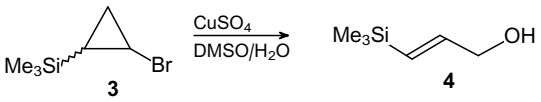
Under analogous conditions (112–117 °C, 2 h), the reaction



1 **2**

of 1-trimethylsilyl-2-bromocyclopropanes **3** [a mixture of *cis* and *trans* isomers (3:1)] also selectively gives only (*E*)-1-trimethylsilylprop-2-en-3-ol **4** (yield 71%).‡

It was shown by quantum-chemical calculations of *Z*- and



3 **4**

E-isomers of both 1-trimethylsilyl-2-bromoprop-2-en-3-ol and 1-trimethylsilylprop-2-en-3-ol (AM1 and PM3 methods[10]) that the *Z*-isomer **2** and the *E*-isomer **4** obtained are the most thermodynamically stable.

It was shown by GLC analysis of the reaction mixtures (0.25×50 m glass capillary column with OV-1701 silicone, 150 °C) that the conversion of the starting halocyclopropanes **1** and **3** under the reaction conditions was complete, and no other low-molecular weight minor products were found in addition to the major products **2** and **4**. Both the starting and the final trimethylsilyl-substituted derivatives are relatively stable compounds, particularly in solution. They are slowly transformed into resinous products at room temperature in 3–4 days.

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† *Spectroscopic data for* **2**: ^{1}H NMR (250 MHz, $CDCl_3$, δ, *J*/Hz): 0.2 (s, 9 H, TMS); 2.36 (br.s, 1 H, OH); 4.2 (d, 2 H, CH_2, *J* 1.25); 6.4 (t, 1 H, CH-$SiMe_3$, *J* 1.25). ^{13}C NMR (73.42 MHz, δ): −0.91 (TMS); 69.90 (C-3); 127.16 (C-1); 140.43 (C-2).

‡ *Spectroscopic data for* **4**: ^{1}H NMR (250 MHz, $CDCl_3$, δ, *J*/Hz): 0.09 (s, 9 H, TMS); 2.15 (s, 1 H, OH); 4.19 (d, 2 H, CH_2, J_2 3.15); 5.71 (d, 1 H, CH-TMS, J_1 13.5); 6.03 (dt, 1 H, C*H*CH_2, J_1 13.5, J_2 3.15). ^{13}C NMR (73.42 MHz, δ): −1.32 (TMS); 65.5 (C-3); 129.65 (C-1); 144.84 (C-2).

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