

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 CuSO₄

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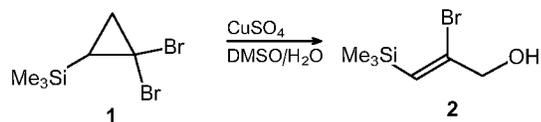
The interaction of 1-bromo- and 1,1-dibromocyclopropanes with an equimolar quantity of CuSO₄ in a DMSO–water mixture (molar ratio halocyclopropane:CuSO₄·5H₂O:DMSO:H₂O = 1:1:10–12:14–16) proceeds *via* cleavage of the three-membered ring to selectively give the most thermodynamically stable isomers of 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.

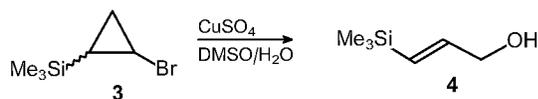
The experiments were conducted with a molar ratio halocyclopropane:CuSO₄·5H₂O:DMSO:H₂O equal to 1:1:10–12:14–16. (*Z*)-1-Trimethylsilyl-2-bromoprop-2-en-3-ol **2** (yield 64%) is selectively formed from 1-trimethylsilyl-2,2-dibromocyclopropane **1** (112–117 °C, 2.5 h).[†]

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



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



E-isomers of both 1-trimethylsilyl-2-bromoprop-2-en-3-ol and 1-trimethylsilylprop-2-en-3-ol (AM1 and PM3 methods¹⁰) 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**: ¹H NMR (250 MHz, CDCl₃, δ, J/Hz): 0.2 (s, 9 H, TMS); 2.36 (br.s, 1 H, OH); 4.2 (d, 2 H, CH₂, J 1.25); 6.4 (t, 1 H, CH-SiMe₃, J 1.25). ¹³C NMR (73.42 MHz, δ): -0.91 (TMS); 69.90 (C-3); 127.16 (C-1); 140.43 (C-2).

[‡] Spectroscopic data for **4**: ¹H NMR (250 MHz, CDCl₃, δ, J/Hz): 0.09 (s, 9 H, TMS); 2.15 (s, 1 H, OH); 4.19 (d, 2 H, CH₂, J₂ 3.15); 5.71 (d, 1 H, CH-TMS, J₁ 13.5); 6.03 (dt, 1 H, CHCH₂, J₁ 13.5, J₂ 3.15). ¹³C NMR (73.42 MHz, δ): -1.32 (TMS); 65.5 (C-3); 129.65 (C-1); 144.84 (C-2).

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