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THE PREPARATION OF THE STERICALLY HINDERED ALCOHOL TRIS(TRIMETHYLSILYL)METHANOL

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Summary

The alcohol $(Me_3Si)_3COH$, with potential for use in the preparation of sterically hindered metal alkoxides, has been prepared by hydrogen peroxide oxidation of the boronic acid $(Me_3Si)_3CB(OH)_2$.

Introduction

There is much current interest in the chemistry of compounds in which metals bear bulky alkoxide ligands; for example, the tri-t-butylmethoxide group has recently been used to prepare the monomeric germanium alkoxide $Ge(OC^tBu_3)_2$ [1]. Our awareness of the interest of several groups in preparing similar derivatives of the alcohol $(Me_3Si)_3COH$, and of several unsuccessful attempts to make it, prompted us to devise a method for its synthesis.

Results and Discussion

Treatment of $(Me_3Si)_3CLi$ with $B(OMe)_3$ gave $(Me_3Si)_3CB(OMe)_2$, this was then partially hydrolysed to a mixture of $(Me_3Si)_3CB(OMe)_2$, $(Me_3Si)_3CB(OH)OMe$ and $(Me_3Si)_3CB(OH)_2$. This mixture was refluxed with a mixture of THF, aqueous H_2O_2 and NaO_2CCH_3, and work up gave a mixture of $(Me_3Si)_3COH$ and $(Me_3Si)_3CH$. The $(Me_3Si)_3COH$ was isolated pure by column chromatography as a low melting solid in 30% yield based on the initial amount of $(Me_3Si)_3CH$ used to prepare the $(Me_3Si)_3CLi$.

Experimental

Preparation of $(Me_3Si)_3COH$. A solution of $B(OMe)_3$ (26.9 g, 0.26 mol) in Et_2O (50 cm^3) was added dropwise to a stirred solution of $(Me_3Si)_3CLi$ (prepared from $(Me_3Si)_3CH$ (20 g, 0.086 mol) and MeLi as described by Aiube and Eaborn [2]) under dry argon at room temperature. After the addition the solution was refluxed for 5 h, during which the solution remained red-brown and a white precipitate formed. The mixture was then added cautiously to H_2O (200 cm^3), which dissolved most of the solid and caused the organic solution to turn pale yellow. The organic layer was separated, washed with water (2 × 50 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure to leave a thick oil, which from its ^1H NMR spectrum appeared to be a mixture of $(Me_3Si)_3CB(OMe)_2$, $(Me_3Si)_3$-$CB(OH)OMe$, $(Me_3Si)_3CB(OH)_2$ and $(Me_3Si)_3CH$. The oil was dissolved in THF (100 cm^3), then 3 *M* NaO_2CCH_3 (10 cm^3) and 100-vol H_2O_2 (11.5 cm^3) were added, and the mixture was refluxed for 24 h then cooled to room temperature. The organic layer was separated, washed with water (2 × 25 cm^3), and dried ($MgSO_4$), and the solvent was removed under reduced pressure to leave an oil, which was a mixture of $(Me_3Si)_3COH$ and $(Me_3Si)_3CH$. The mixture was separated by column chromatography using silica gel (60–120 mesh) with 1/1 v/v hexane/CH_2Cl_2 as eluent to give $(Me_3Si)_3COH$ (7.5 g; 30%, based on $(Me_3Si)_3CH$ taken), m.p. 35°C, (Found: C, 48.2; H, 10.9. $C_{10}H_{28}OSi_3$ calcd.: C, 48.3; H, 11.35%); δ(H) ($CDCl_3$ solution, 360 MHz): 0.11 (s, 27H, $SiMe_3$) and 0.45 ppm (br.s, 1H, OH) (the resonance at 0.45 ppm disappeared on shaking the solution with D_2O); δ(C) ($CDCl_3$ solution): 0.31 (Me) and 57.69 ppm (COH). Mass spectrum (EI): *m/z* 233 (5%, $[M-Me]^+$), 217 (7, $[M-MeO]^+$), 159 (10, $[M-Me_3SiO]^+$), 147 (30, $[Me_3SiOSiMe_2]^+$), 143 (35, $[M-Me_3SiOH\text{-}Me]^+$), 133 (25, $[Me_3SiOSiMeH]^+$), 75 (20, $[Me_2SiOH]^+$), 73 (100, $[Me_3Si]^+$).

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