Synthese und Cyclisierung von Boryl- und Silylhydrazonen

Synthesis and Cyclisation of Boryl- and Silylhydrazones

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Z. Naturforsch. **2010**, *65b,* 587 – 602; received November 18, 2009

Professor Gerhard Roewer zum 70. Geburtstag gewidmet

Reactions of the lithium salts of the *tert*-butylmethylhydrazones $Me_3C(Me)C{=}N{-}NLiR$, (R = H, Me, CMe_3) with fluorosilanes and -boranes in a molar ratio 1 : 1 gave the silyl- (**1** – **3**, **5**, **6**) and borylhydrazones (**4**, **8**) $Me_3C(Me)C{=}N{-}N(R)R'$; **1**: R = H, R′ = $SiFMe_2$; **2**: R = H, R′ = $SiMe_2CMe_3$; **3**: R = H, R′ = $SiF(CMe_3)_2$; **4**: R = H, R′ = $BFN(SiMe_3)_2$; **5**: R = Me_3C, R′ = SiF_2CMe_3; **6**: R = Me_3C, R′ = $F_2SiC(SiMe_3)_3$; **8**: R = Me_3C, R′ = $BFN(SiMe_3)_2$. The lithiated hydrazone $Me_2C{=}N{-}NH(Me)$ reacted with $F_3SiC(SiMe_3)_3$ to give the silylhydrazone $Me_2C{=}N{-}NHSiF_2C(SiMe_3)_3$, **7**. Because of the fluoro functionality of **1** and **4**, the bis-hydrazonylsilane **9** and the bis- and tris-hydrazonylboranes **10** and **11** could be synthesised, $(Me_3C(Me)C{=}N{-}NH)_2R$; **9**: R = $SiMe_2$, **10**: R = $BN(SiMe_3)_2$; **11**: $(Me_3C(Me)C{=}N{-}NH)_3B$. Starting from **2** and its lithium salt, secondary substitutions are possible. Bis(silyl)- and silyl(boryl)hydrazones are formed (**12** – **15**); $Me_3C(Me)C{=}N(R)$ ($SiMe_2CMe_3$) **12**: R = $SiFMe_2$; **13**: R = $SiF(CMe_3)_2$; **14**: R = SiF_2CMe_3; **15**: R = $BFN(SiMe_3)_2$. Ring closure occurs in the reaction of dilithiated $Me_2C{=}N{-}NHCMe_3$ with $F_2Si(CHMe_2)_2$. The 1,2-diaza-3-sila-5-cyclopentene **16** is isolated. The fluorofunctional silyl-hydrazones **7**, **12**, and **13** cyclise in reactions with *t*-BuLi to give 1,2-diaza-3-sila-5-cyclopentenes **17** – **20**; $RN(N{=}CR'{-}CH_2)R''$; **17**: R = Me, R′ = Me_3C, R″ = $SiFC(SiMe_3)_3$; **18**: R = Me_3C, R′ = $SiMe_2CMe_3$, R″ = $SiMe_2$; **19**: R = Me_3C, R′ = $SiMe_2CMe_3$, R″ = $Si(CMe_3)_2$. A 1,2-diaza-3-bora-5-cyclopentene **20** is the result of the reaction of **8** with *t*-BuLi: $Me_3CN(N{=}CCMe_3{-}CH_2)BN(SiMe_3)_2$. The H-acidic methylene group of the five-membered ring in **20** can be lithiated with *n*-BuLi and substituted with fluorosilanes. Starting from **16** and **20**, the silyl-substituted rings $Me_3CN(N{=}CMe{-}CHR)Si(CHMe_2)_2$ **21** – **23** and **25** are obtained; **21**: R = $SiMe_3$; **22**: R = $SiF_2C(SiMe_3)_3$; **23**: R = SiF_3; **25**: $Me_3CN[N{=}CC(Me)_3CHSiMe_3]BN(SiMe_3)_2$. Using SiF_4 as fluorosilane, the main product is the difluorosilane containing two rings; $F_2Si[CHC(Me){=}N{-}NCMe_3{-}Si(CHMe_2)_2]_2$. The methine group in 4-position of the silyl-substituted rings is also acidic and reacts with *n*-BuLi to give lithium salts which react with aminodifluoroboranes giving the ring compounds $Me_3CN[N{=}C(CMe_3)C(SiMe_2R)(FBNR'SiMe_3)]SiMe_2$ **26** – **28**; **26**: R = Me, R′ = CMe_3; **27**: R = F, R′ = CMe_3; **28**: R = F, R′ = $SiMe_3$. In contrast to the substitution reactions of fluorosilanes with lithiated rings, an unusual oxidation reaction occurs starting from lithiated $Me_3CN(N{=}C(CMe_3)CH_2)Si(CHMe_2)_2$ and $ClSiMe_2CMe_3$ to give **29**, in which a C–C bond in 4-position links two five-membered rings. The disilane $(Me_3CSiMe_2)_2$ is formed as a by-product of this reaction. The combination of the N-SiF_2CMe_3-substituted hydrazones **5** and **14** with *t*-BuLi in a molar ratio 1 : 2 leads to the colourless, crystalline tricyclic products **30** and **31** which are dimeric 1,2-diaza-3-sila-3,5-cyclopentadienes. The molecular structures of **3**, **6**, **11**, **30**, and **31** are reported.

Key words: Borylhydrazone, Silylhydrazone, Diazasilacyclopentene, Diazaboracyclopentene, Diazasilacyclopentadiene, One-electron Oxidation