Synthese von Fluorsilylenolaten, Aminosilylenolaten, -ethern und Aldolkondensaten

Synthesis of Fluorosilylenolates, Aminosilylenolates, -ethers, and Aldol Condensates

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Depending on the reaction conditions, ketones react with *n*-BuLi, *tert*-BuLi or lithium diisopropylamide to give enolates or alcoholates. In the reaction of *tert*-butylmethylketone with *n*-BuLi followed by fluorosilanes, the fluorosilyl-enolates $H_2C{=}C(O{-}SiFRR')CMe_3$ (**1** – **4**) and fluorosilylethers $Me_3C(CH_3)(n\text{-}C_4H_9)C{-}O{-}SiFRR'$ (**5** – **8**) [R, R′ = Me (**1**, **5**); F, CMe_3 (**2**, **6**); F, C_6H_5 (**3**, **7**); F, $CHMe_2$ (**4**, **8**)] are formed. Using *tert*-butylmethylketone, *n*-BuLi and $(Me_3C)_2SiF_2$, isobutene and the fluorosilyl-enolate of acetaldehyde $H_2C{=}CH{-}O{-}SiF(CMe_3)_2$ (**9**) are obtained. Diisopropylketone reacts with Me_3CLi and fluorosilanes to give the fluorosilyl-enolates $Me_2C{=}C(O{-}SiFRR')CHMe_2$ (**10**, **11**) and -ethers, $Me_3C(Me_2HC)_2C{-}O{-}SiFRR'$ (**12**, **13**) [R, R′ = Me (**10**, **11**); F, CMe_3 (**12**, **13**)] whereas only the silylethers $R(Me)(C_6H_5)C{-}O{-}SiFRR'$ [R, R′, R″ = *n*-C_4H_9, Me, Me (**14**); C_6H_5, F, Me (**15**)] are generated in the reaction of $H_3C(C_6H_5)C{=}O$ with lithium-alkyls and fluorosilanes. 1-Di(*tert*-butyl)fluorosiloxy-1-cyclohexene (**16**) is the product of the reaction of lithiated cyclohexanone and $(Me_3C)_2SiF_2$. A side reaction of the enolate formation is often a condensation releasing water. For that reason, acyclic and cyclic siloxanes may appear as by-products, *e. g*. disiloxane (**17**) using $(Me_3C)_2SiF_2$, cyclotrisiloxane $(Me_3C(C_6H_5)Si{-}O)_3$ (**18**) using $Me_3(C_6H_5)SiF_2$, or cyclotetrasiloxane $(Me_3CSiF{-}O)_4$ (**19**) using Me_3CSiF_3 in these reactions. Attempts to prepare the enolate of cyclopentanone in the reaction with lithium diisopropylamide lead to the formation of 2,5-dicyclopentylidenepentanone (**20**). The 3,5,7-triphenyl-3-methyl-4,6-hexadienephenone (**21**) is an aldol condensate of $Me(C_6H_5)CO$. Lithium-*tert*-butylmethylenolate reacts with fluorosilyl-enolates **1** – **3** or SiF_4 to give bis(enolato)silanes, $(H_2C{=}C(CMe_3)O{-})_2SiRR'$ [R, R′ = Me (**22**); F, CMe_3 (**23**); F, C_6H_5 (**24**);] and the tris(enolato)silanes $(H_2C{=}C(CMe_3)O{-})_3SiR$ [R = C_6H_5 (**25**); F (**26**)]. Aminosilyl-enolates $H_2C{=}C(O{-}SiR'R''{-}NHR)CMe_3$ are obtained in reactions of fluorosilyl-enolates with lithium amide [**27**: R= CMe_3, R′= Me, R″= Me; **28**: R= C_6H_5, R′= F, R″= CMe_3;]. Results of the crystal structure determinations of **17**, the *cis*-isomer of **18**, one *trans*-isomer of **19**, the pentanone **20**, and the hexadienephenone **21** are reported.

Key words: Keto-Enol Tautomerism, Fluorosilylenolates, Fluorosilylethers, Aldol Condensates, Cyclosiloxanes