Journal of Organometallic Chemistry, 406 (1991) 87–89
Elsevier Sequoia S.A., Lausanne
JOM 21363

A novel synthetic route to 1-aza-2-silacyclopentane derivatives

M.G. Voronkov, S.V. Kirpichenko, A.T. Abrosimova and A.I. Albanov
Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, 664033 Irkutsk (USSR)

(Received August 26th, 1990)

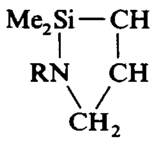
Abstract

$Me_2HSiCH_2CH_2CH_2Cl$ reacts with primary alkyl, aryl or aralkyl amines to form the corresponding 1-aza-2-silacyclopentanes $Me_2\overline{SiCH_2CH_2CH_2N}R$. It seems that the ease of ring closure is a result of enhanced reactivity of the Si–H bond of the intermediate $[Me_2HSiCH_2CH_2CH_2NHR]$ arising from intramolecular Si $\cdots$ N interaction.

Dehydrocondensation of trialkylhydrosilanes with amines proceeds in the presence of heterogeneous or homogeneous catalysts [1,2]. Alkali metal amides are also used as catalysts for this reaction [3]. At this point the formation of 1-phenyl-2,2-dimethyl-1-aza-2-silacyclopentane (IIIa) upon heating of dimethyl(3-chloropropyl)silane (I) with aniline seems to be unexpected. The reactions of I with benzylamine and methylamine occur in a similar way to give the corresponding 1-aza-2-silacyclopentane derivatives. In the case of methylamine, bis(3-dimethylsilylpropyl)amine, $(HMe_2SiCH_2CH_2CH_2)_2NMe$ is obtained as the by-product.

It is likely that the initial step of these reactions involves a nucleophilic attack at the CH_2Cl group yielding dimethyl(3-organylaminopropyl)silane (II). However, the latter compound is not observed in the reaction mixture. The intramolecular reaction between the Si–H and N–H groups of II takes place resulting in ring closure and the formation of a cyclic product.

$$\underset{\text{(I)}}{HMe_2SiCH_2CH_2CH_2Cl} + RNH_2 \longrightarrow \underset{\text{(IIa–c)}}{[HMe_2SiCH_2CH_2CH_2NHR]} \longrightarrow$$



(IIIa–c)

(R = Ph (a); $PhCH_2$ (b); Me (c))

0022-328X/91/$03.50

In contrast, the intramolecular dehydrocondensation of compounds of the type $Me_2HSiCH_2CH_2CH_2XH$ (X = O, S) occurs only under catalytic conditions [4,5]. It is probable that the ease of ring closure of compounds with X = NR is due to the ability of the nitrogen atom to coordinate intramolecularly with the silicon atom which leads to activation of the Si–H bond [6,7]. The enhancement of reactivity of the Si–H bond towards nucleophiles was observed previously in the case of (3-dimethylaminopropyl)silane derivatives and pentacoordinate silicon compounds with the intramolecular Si ··· N bond [8,9].

Experimental

All reactions were carried out in a stainless autoclave. NMR spectra were recorded on a JEOL FX 90Q at 90 MHz with $CDCl_3$ as a solvent. Cyclohexane was used as an internal standard.

Preparation of compounds

A mixture of $Me_2HSiCH_2CH_2CH_2Cl$ (0.037 mol) and amine (0.111 mol) was heated at 120 °C for 7 h. After cooling, the precipitate of amine hydrochloride was filtered off, washed several times with dry ether and the solution obtained was distilled under atmospheric or reduced pressure.

IIIa * (yield 47%), b.p. 102 °C/2 Torr. Found: C, 69.01; H, 8.98; Si, 14.75. $C_{11}H_{17}NSi$ calcd.: C, 69.04; H, 8.96; Si, 14.68%. ^1H NMR: δ 0.32 (s, 6H, CH_3Si); 0.81 (t, 2H, CH_2Si); 1.94 (quint, 2H, $C{-}CH_2{-}C$); 3.16 (t, 2H, CH_2N); 6.73–7.18 (m, 5H, C_6H_5). ^{29}Si NMR: δ +15.29.

IIIb (yield 21%), b.p. 90 °C/1 Torr. Found: C, 69.99; H, 9.07; Si, 13.41. $C_{12}H_{19}NSi$ calcd.: C, 70.18; H, 9.33; Si, 13.68%. ^1H NMR: δ 0.09 (s, 6H, CH_3Si); 0.72 (t, 2H, $SiCH_2$); 1.81 (quint, 2H, $C{-}CH_2{-}C$); 2.73 (t, 2H, NCH_2); 3.96 (s, 2H, CH_2Ph); 7.26 (m, 5H, C_6H_5).

IIIc * (yield 48%), b.p. 115 °C. Found: C, 55.66; H, 11.79; Si, 21.65. $C_6H_{15}NSi$ calcd.: C, 55.74; H, 11.70; Si, 21.72%. ^1H NMR: δ 0.06 (s, 6H, CH_3Si); 0.69 (t, 2H, CH_2Si); 1.84 (quint, 2H, $C{-}CH_2{-}C$); 2.52 (s, 3H, CH_3N); 2.77 (t, 2H, CH_2N). ^{29}Si NMR: δ +15.0.

IVc (yield 26%), b.p. 88–90 °C/1 Torr. Found: C, 57.17; H, 12.61; N, 6.66; Si, 23.83. $C_{11}H_{29}NSi_2$ calcd.: C, 57.06; H, 12.62; N, 6.05; Si, 24.26%. ^1H NMR: δ 0.09 (d, 6H, CH_3Si; 0.57 (m, 2H, CH_2Si); 1.52 (m, 2H, $C{-}CH_2{-}C$); 2.22 (s, 3H, CH_3N); 2.34 (m, 2H, CH_2N); 3.89 (m, 1H, SiH).

References

1 L.H. Sommer and J.D. Citron, J. Org. Chem., 32 (1967) 2470.
2 K.A. Andrianov, M.I. Filimonova and V.I. Sidorov, J. Organomet. Chem., 142 (1977) 31.
3 B.N. Dolgov, N.P. Haritonov and M.G. Voronkov, Zh. Obsh. Khim., 24 (1954) 678.
4 R.J.P. Corriu and C. Guérin, Tetrahedron, 37 (1981) 2467.
5 R.J.P. Corriu, J.M. Fernandez, C. Guérin and A. Kpoton, Bull. Soc. Chim. Belg., 89 (1980) 783.

---

* Previously compounds IIIa and IIIc were prepared from dimethyl(3-chloropropyl)chlorosilane and the corresponding amine [10].

6 I.E. Saratov, I.V. Shpak and V.O. Reikhsfel'd, Zh. Obsh. Khim., 51 (1980) 2030.
7 R.J.P. Corriu, R. Perz and C. Reye, Tetrahedron, 39 (1983) 999.
8 I.E. Saratov, I.V. Shpak and V.O. Reikhsfel'd, Zh. Obsh. Khim., 51 (1981) 396.
9 J. Boyer, C. Breliere, R.J.P. Corriu, A. Kpoton, M. Poirier and G. Royo, J. Organomet. Chem., 311 (1986) C39.
10 J.L. Speier, Fr. 1,335,705; Chem. Abstr., 60 (1964) 1794.