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SHORT COMMUNICATIONS

Reaction of 2,3,5,10b-Tetrahydrooxazolo[3,2-*c*][1,3]benzoxazines with Chlorotrimethylsilane

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Cleavage of oxazolidines (which may be regarded as five-membered N,O-acetals) with halotrimethylsilanes is known to give silylated alcohols containing, depending on the oxazolidine structure, enamine or imine fragments [1, 2]. These alcohols are often used as intermediate products in the synthesis of more complex nitrogen- and silicon-containing compounds [2, 3].

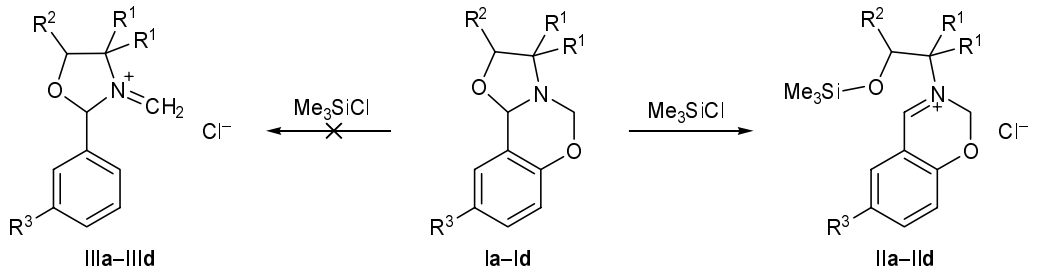
In the present communication we report for the first time on the reaction of 2,3,5,10b-tetrahydrooxazolo-[3,2-*c*][1,3]benzoxazines **Ia**–**Id** with chlorotrimethylsilane. The reactions were carried out with equimolar amounts of the reactants in benzene at room temperature. The yield of 3-(2-trimethylsilyloxyalkyl)-2*H*-1,3-benzoxazinium chlorides **IIa**–**IIc** was almost quantitative. In the case of 3,3-dimethyl derivative **Id**, heating of the reaction mixture for 5 h under reflux was necessary to obtain salt **IId** in a good yield (93%).

The presence in molecules **Ia**–**Id** of two N,O-acetal rings (five- and six-membered) assumes the possibility for the reaction with chlorotrimethylsilane to occur at both rings or only one of these, e.g., with formation of compounds **IIIa**–**IIId**. However, in all cases the reaction was strictly regioselective, and only the oxazolidine ring was opened. Presumably, unlike compounds **IIIa**–**IIId**, the newly formed double bond in structure **II** is conjugated with the benzene ring.

The ^{1}H NMR spectra of compounds **IIa**–**IId** contained singlets from protons of the N=CH and NCH_2O groups or doublets of doublets from the NCH_2O protons in compounds with an asymmetric carbon atom (**IIb** and **IIc**); no signals assignable to $N{=}CH_2$ group were present.

3-(2-Trimethylsilyloxyalkyl)-2*H*-1,3-benzoxazinium chlorides IIa–IId (*general procedure***).** Chlorotrimethylsilane, 0.1 mol, was added dropwise to a solution of 0.1 mol of 2,3,5,10b-tetrahydrooxazolo-[3,2-*c*][1,3]benzoxazine **Ia**–**Id** in 100 ml of benzene under stirring at room temperature. The precipitate was filtered off and dried under reduced pressure.

6-Bromo-3-(2-trimethylsilyloxyethyl)-2*H*-1,3-benzoxazinium chloride (IIa). Yield 98%, mp 84–86°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.06 s (9H, $SiMe_3$), 3.34 t (2H, NCH_2, ^3J = 6.8), 4.04 t (2H, OCH_2, ^3J = 6.8), 4.69 s (2H, NCH_2O), 6.96 d (1H, 8-H, $^3J_{7,8}$ = 8.9), 7.68 d.d (1H, 7-H, $^4J_{5,7}$ = 2.5, $^3J_{7,8}$ = 8.9), 7.86 d (1H, 5-H, $^4J_{5,7}$ = 2.5), 9.91 s (1H, N=CH). Found, %: C 42.66; H 5.17; Br 21.97; Cl 9.64; N 3.71;



$R^1 = R^2 = H$, R^3 = Br (**a**); R^1 = H, R^2 = Me, R^3 = Br (**b**); R^2 = Me, $R^1 = R^3 = H$ (**c**); R^1 = Me, $R^2 = R^3 = H$ (**d**).

Si 7.58. $C_{13}H_{19}BrClNO_2Si$. Calculated, %: C 42.81; H 5.25; Br 21.91; Cl 9.72; N 3.84; Si 7.70.

6-Bromo-3-(2-trimethylsilyloxypropyl)-2*H*-1,3-benzoxazinium chloride (IIb). Yield 97%, mp 110–112°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.06 s (9H, $SiMe_3$), 1.29 d (3H, Me, ^3J = 6.12), 2.71 d.d (1H, NC**H**$_A$H$_B$CH$_X$, $^3J_{AX}$ = 8.4, $^2J_{AB}$ = 10.8), 3.47 d.d (1H, NCH$_A$**H**$_B$CH$_X$, $^3J_{BX}$ = 6.3, $^2J_{AB}$ = 10.8), 4.17 m (1H, NCH$_A$H$_B$C**H**$_X$, $^3J_{1,2}$ = 6.1, $^3J_{BX}$ = 6.3, $^3J_{AX}$ = 8.4), 4.47 d (1H, OC**H**$_A$H$_B$N, $^2J_{AB}$ = 5.5), 4.89 d (1H, OCH$_A$**H**$_B$N, $^2J_{AB}$ = 5.5), 7.09 d (1H, 8-H, $^3J_{7,8}$ = 8.8), 7.64 d.d (1H, 7-H, $^4J_{5,7}$ = 2.7, $^3J_{7,8}$ = 8.8), 7.71 d (1H, 5-H, $^4J_{5,7}$ = 2.7), 10.23 s (1H, N=CH). Found, %: C 44.53; H 5.47; Br 21.01; Cl 9.45; N 3.54; Si 7.52. $C_{14}H_{21}BrClNO_2Si$. Calculated, %: C 44.39; H 5.59; Br 21.10; Cl 9.36; N 3.70; Si 7.41.

3-(2-Trimethylsilyloxypropyl)-2*H*-1,3-benzoxazinium chloride (IIc). Yield 97%, mp 101–103°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.06 s (9H, $SiMe_3$), 1.32 d (3H, Me, $^3J_{1,2}$ = 6.12), 2.77 d.d (1H, NC**H**$_A$H$_B$CH$_X$, $^3J_{AX}$ = 8.64, $^2J_{AB}$ = 10.92), 3.47 d.d (1H, NCH$_A$**H**$_B$CH$_X$, $^3J_{BX}$ = 6.16, $^2J_{AB}$ = 10.92), 4.17 d.d.d (1H, NCH$_A$H$_B$C**H**$_X$, $^3J_{1,2}$ = 6.12, $^3J_{BX}$ = 6.16, $^3J_{AX}$ = 8.64), 4.52 d (1H, OC**H**$_A$CH$_B$N, $^2J_{AB}$ = 5.4), 4.92 d (1H, OCH$_A$C**H**$_B$N, $^2J_{AB}$ = 5.4), 6.95 d.d.d (1H, 6-H, $^4J_{6,8}$ = 0.8, $^3J_{6,7}$ = 7.2, $^3J_{6,5}$ = 7.7), 7.07 d.d (1H, 8-H, $^4J_{6,8}$ = 0.8, $^3J_{7,8}$ = 8.3), 7.51 d.d.d (1H, 7-H, $^4J_{5,7}$ = 1.8, $^3J_{6,7}$ = 7.2, $^3J_{7,8}$ = 8.3), 7.66 d.d (1H, 5-H, $^4J_{5,7}$ = 1.8, $^3J_{5,6}$ = 7.7), 10.27 s (1H, N=CH). Found, %: C 56.19; H 7.46; Cl 11.66; N 4.53; Si 9.45. $C_{14}H_{22}ClNO_2Si$. Calculated, %: C 56.08; H 7.39; Cl 11.82; N 4.67; Si 9.37.

3-(1,1-Dimethyl-2-trimethylsilyloxyethyl)-2*H*-1,3-benzoxazinium chloride (IId). Yield 93%, mp 86–87°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.07 s (9H, $SiMe_3$), 1.46 s (6H, 2Me), 3.57 s (2H, OCH_2C), 4.61 s (2H, OCH_2N), 7.08 d.d.d (1H, 6-H, $^4J_{6,8}$ = 0.5, $^3J_{6,7}$ = 7.2, $^3J_{6,5}$ = 7.9), 7.23 d.d (1H, 8-H, $^4J_{6,8}$ = 0.5, $^3J_{7,8}$ = 8.2), 7.67 d.d.d (1H, 7-H, $^4J_{5,7}$ = 1.6, $^3J_{6,7}$ = 7.2, $^3J_{7,8}$ = 8.2), 8.06 d.d (1H, 5-H, $^4J_{5,7}$ = 1.6, $^3J_{5,6}$ = 7.9), 9.37 s (1H, N=CH). Found, %: C 57.53; H 7.89; Cl 11.34; N 4.31; Si 8.82. $C_{15}H_{24}ClNO_2Si$. Calculated, %: C 57.40; H 7.71; Cl 11.29; N 4.46; Si 8.95.

The ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) at 26°C from solutions in DMSO-d_6 using HMDS as internal reference. Freshly distilled commercial chlorotrimethylsilane was used. 2,3,5,10b-Tetrahydrooxazolo[3,2-*c*][1,3]benzoxazines **Ia**–**Id** were synthesized by the procedure reported in [4]; their purity was no less than 96% (according to the GLC data).

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