

SHORT
COMMUNICATIONS

Reactions of 2-(2-Furyl)-1,3-dioxacycloalkanes with Triethylsilane

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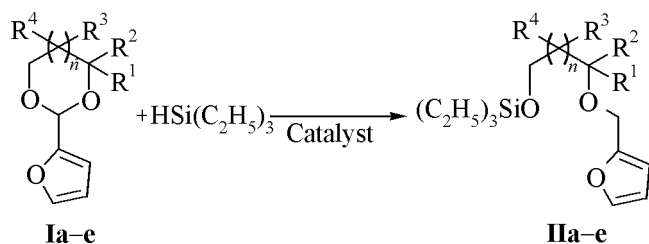
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1,3-Dioxacycloalkanes react with triethylsilane in the presence of various catalysts furnishing products of heterocycle cleavage at the C–O bond of the acetal site, alkoxy(triethylsiloxy)alkanes [1, 2] possessing high biological activity, often greater than that of their cyclic precursors [3]. The target of this work was to study the behavior in this reaction of biologically active [4] furyl-substituted 1,3-dioxacycloalkanes and to prepare their silicon-containing derivatives.

We were the first to investigate the reaction with triethylsilane of 2-(2-furyl)-1,3-dioxacycloalkanes **Ia–e** in the presence of zinc halides, reduced nickel, and metal complex catalyst, dicyclopentadienylzirconium dichloride Cp₂ZrCl₂. By the reaction were synthesized previously unknown α-triethylsiloxy-ω-furfuryloxyalkanes **IIa–e**.



$n = 0$ (**Ia**, **IIa**), 1 (**Ib–e**, **IIb–e**), $R^1 = \text{H}$ (**Ia–c**, **e**, **IIa–c**, **e**), CH_3 (**Id**, **IIId**), $R^2 = \text{H}$ (**Ia**, **b**, **e**, **IIa**, **b**, **e**), CH_3 (**Ic**, **d**, **IIc**, **d**), $R^3 = \text{H}$ (**Ib–d**, **IIb–d**), CH_3 (**Ie**, **IIe**), $R^4 = \text{H}$ (**Ib–d**, **IIb–d**), CH_3 (**Ie**, **IIe**); catalyst ZnCl_2 , ZnI_2 , AlCl_3 , Ni , Cp_2ZrCl_2 .

We established that the best catalyst was Cp₂ZrCl₂: Applied in amount of 1 mol% it ensured within 0.5–1 h at 70°C almost complete conversion of initial compounds **Ia–e** and close to quantitative yield of

target products **IIa–e**. Somewhat worse were the results with reduced nickel as catalyst (2 mol%): In its presence in 1–1.5 h at 100–110°C the yield of compounds **IIa–e** attained 75–82%. The use as catalyst of Lewis acids (ZnCl_2 , ZnI_2 , AlCl_3) in 2–5 mol% quantity turned out to be unsuitable in this reaction because of low selectivity and a trend of compounds **Ia–e** to hydrolyze and undergo tarring in acid medium at high temperature (120–130°C). The yield of compounds **IIa–e** under these conditions did not exceed 30%.

Procedure for preparation of α-triethylsiloxy-ω-furfuryloxyalkanes IIa–e. Into a air-tight glass reactor equipped with a jacket connected to a thermostat, magnetic stirrer, and a device for sampling was charged 0.05 mol of 1,3-dioxacycloalkanes **Ia–e**, 0.05 mol (5.8 g) of triethylsilane, and 1 mol% (0.146 g) of dried Cp₂ZrCl₂ (from a sealed ampule or a desiccator). The mixture was stirred at 70°C for 0.5–1 h. The reaction product was separated by vacuum distillation.

1-Triethylsiloxy-2-(furfuryloxy)ethane (IIa). Yield 97%, bp 82°C (4 mm Hg), d_4^{20} 0.8812, n_D^{20} 1.4424. ¹H NMR spectrum, δ, ppm: 3.20 s (2H, furyl-CH₂O), 3.40 t (2H, CH₂CH₂O), 3.66 t (2H, CH₂OSi). Found, %: C 60.7; H 9.41; Si 11.01. C₁₃H₂₄O₃Si. Calculated, %: C 60.91; H 9.37; Si 10.97. *M* 256.1.

1-Triethylsiloxy-3-(furfuryloxy)propane (IIb). Yield 98%, bp 98°C (3 mm Hg), d_4^{20} 0.8844, n_D^{20} 1.4463. ¹H NMR spectrum, δ, ppm: 1.72 m (2H, CH₂CH₂CH₂), 3.22 s (2H, furyl-CH₂O), 3.43 t (2H, CH₂CH₂O), 3.62 t (2H, CH₂OSi). Found, %: C 62.5; H 9.68; Si 10.35. C₁₄H₂₆O₃Si. Calculated, %: C 62.2; H 9.63; Si 10.4. *M* 270.1.

1-Triethylsiloxy-3-methyl-3-(furfuryloxy)propane (IIc). Yield 97%, bp 115°C (4 mm Hg), d_4^{20} 0.8866, n_D^{20} 1.4468. ^1H NMR spectrum, δ , ppm: 1.12 d (3H, CH_3), 1.58 m [2H, $\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2$], 3.23 s (2H, furyl- CH_2O), 3.40 m (1H, OCHCH_3), 3.63 t (2H, CH_2OSi). Found, %: C 63.41; H 9.9; Si 9.9. $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}$. Calculated, %: C 63.36; H 9.85; Si 9.89. *M* 284.1.

1-Triethylsiloxy-3,3-dimethyl-3-(furfuryloxy)propane (II d). Yield 95%, bp 123°C (3 mm Hg), d_4^{20} 0.8912, n_D^{20} 1.4459. ^1H NMR spectrum, δ , ppm: 1.05 s (6H, 2CH_3), 1.60 m [2H, $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$], 3.20 s (2H, furyl- CH_2O), 3.40 m (1H, OCHCH_3), 3.63 t (2H, CH_2OSi). Found, %: C 64.5; H 10.1; Si 9.52. $\text{C}_{16}\text{H}_{30}\text{O}_3\text{Si}$. Calculated, %: C 64.41; H 10.06; Si 9.43. *M* 298.1.

1-Triethylsiloxy-2,2-dimethyl-3-(furfuryloxy)propane (IIe). Yield 98%, bp 132°C (4 mm Hg), d_4^{20} 0.8932, n_D^{20} 1.4448. ^1H NMR spectrum, δ , ppm: 0.89 s (6H, 2CH_3), 1.60 m [2H, $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$], 3.02 s [2H, $\text{OCH}_2\text{C}(\text{CH}_3)_2$], 3.21 s (2H, furyl- CH_2O), 3.35 s (2H, CH_2OSi). Found, %: C 64.48; H 10.11; Si 9.4. $\text{C}_{16}\text{H}_{30}\text{O}_3\text{Si}$. Calculated, %: C 64.41; H 10.06; Si 9.43. *M* 298.1.

Alongside the resonances listed above in all ^1H NMR spectra of compounds obtained are present the signals from methyl and methylene protons belonging to triethylsilyl groups at 0.5 and 0.9 ppm respectively, and also multiplets at 6.25–6.35 ppm (2H, 2CH) and 7.34–7.40 ppm (1H, CH) corresponding to the furyl moiety.

^1H NMR spectra were registered on spectrometer Tesla BS-467 (100 MHz) at 24–26°C from solutions in CCl_4 , internal reference HMDS.

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