Synthesis of Silyl, Germyl, and Stannyl Alk-1-ynyl Ketones from 2-Lithio-2-(trimethylsilylethynyl)-1,3-dioxan

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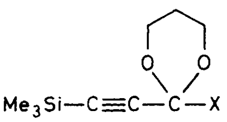
The ketones R–C≡C–CO–MMe$_3$ (M = Si, Ge, Sn; R = SiMe$_3$, Bu^t) have been prepared from 1,3-dioxan-2-yl acyl anion equivalents.

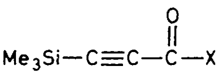
Alk-1-ynyl silyl ketones are starting materials for the preparation of silyl ethers of enols, dienols, and allenols.[1] Alk-1-ynyl germyl ketones and alk-1-ynyl stannyl ketones are, to our knowledge, unknown. Earlier attempts to hydrolyse stannyl 1,3-dithians failed[2] thereby excluding the dithian method as an approach to stannyl ketones. Unlike 1,3-dithians the dioxans (**1**) can be hydrolysed under very mild conditions.

Treatment (3 h; −65 °C, then slowly warmed to room temp.) of a solution of (**1b**) [obtained from (**1a**) and Bu^{n}Li (tetrahydrofuran–hexane, 5:2; −65 °C; 30 min)] with Me$_3$MCl (M = Si, Ge, Sn) gave (**1c**) (70% yield after aqueous work-up and distillation), (**1d**) (28%), and (**1e**) (76%). For the silyl compound, 10% hexamethylphosphoric triamide was added prior to addition of the chloride. The allenic isomer was present in the crude mixture in the germanium case but did not survive the work-up conditions. Hydrolysis [acetone–water, 4:1; 0.01 M-H$_2$SO$_4$; room temp.; (**1c, d**) 10 h; (**1e**) 30 min] yielded the ketones† (**2a**) (84%), (**2b**) (68%), and (**2c**) (70%). With atmospheric oxygen (**2c**) was rapidly oxidized[3] to the stannoic ester (**2d**).



(1)

a; X = H
b; X = Li
c; X = SiMe$_3$
d; X = GeMe$_3$
e; X = SnMe$_3$



$Me_3Si{-}C{\equiv}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}X$

(2)

a; X = SiMe$_3$
b; X = GeMe$_3$
c; X = SnMe$_3$
d; X = OSnMe$_3$

Similar transformations were carried out starting with 2-(3,3-dimethylbut-1-ynyl)-1,3-dioxan.

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References

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† Yields are those following chromatography (**2a, b**), or distillation, (**2c**): (**2a**): λ_{max} 224 nm (ϵ 8529); ν_{max} 2135 and 1600 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 0.29; ^{13}C n.m.r. (CDCl$_3$) δ 227.1, 107.3, 104.7, −0.7, and −3.7 p.p.m.; (**2b**) λ_{max} 222 nm (ϵ 11 086); ν_{max} 2130 and 1610 cm^{-1}; δ(^{1}H) 0.44 and 0.29; δ(^{13}C) 227.5, 108.9, 103.6, −0.7, and −3.2 p.p.m.; (**2c**) λ_{max} 225 nm (ϵ 8549); ν_{max} 2120 and 1600 cm^{-1}; δ(^{1}H) 0.40 and 0.31; δ(^{13}C) 236.8, 112.3, 104.7, −0.7, and −8.8 p.p.m.