Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

GERMANOTROPIC EQUILIBRIUM

I. F. LUTSENKO, YU. I. BAUKOV, I. YU. BELAVIN AND A. N. TVOROGOV
Chemistry Department, Moscow State University "M.V.Lomonosov" Moscow (U.S.S.R.)

(Received April 23rd, 1968)

This paper presents data on the preparation of isomeric organogermanium *O*- and *C*-derivatives of acetone and on the equilibria, controlling their mutual transformations. When tripropylstannylacetone was treated with trimethylbromogermane an exothermic reaction took place. The reaction mixture was distilled and the fraction boiling in the range 40–90° (80 mm) was isolated. After further distillation this fraction gave a mixture of *C*- and *O*-germylation products (yields 65%, b.p. 85–95° (100 mm), n_D^{20} 1.4419).

$$\mathrm{Me_3GeBr} \xrightarrow[-\mathrm{Pr_3SnBr}]{+\mathrm{Pr_3SnCH_2COCH_3}} \mathrm{Me_3GeCH_2COCH_3} + \mathrm{Me_3GeOC(CH_3){=}CH_2}$$

The *O*-isomer content of the distillate was shown by NMR to be 10%. The structure of the reaction products was established by infrared and NMR spectroscopy: $\mathrm{Me_3GeCH_2COCH_3}$, $\nu(\mathrm{C{=}O})$ 1696 $\mathrm{cm^{-1}}$, $\delta(\mathrm{CH_2})$ 2.2, $\delta(\mathrm{CH_3})$ 1.97, $\delta(\mathrm{GeCH_3})$ 0.25 ppm, $J(\mathrm{CH_2COCH_3}) \sim 0.6$ Hz; $\mathrm{Me_3GeOC(CH_3){=}CH_2}$, $\nu(\mathrm{C{=}C})$ 1645, $\nu(\mathrm{CH_2})$ 3100 $\mathrm{cm^{-1}}$, $\delta(\mathrm{CH_2})$ 3.72, 3.8, $\delta(\mathrm{CH_3})$ 1.66, $\delta(\mathrm{GeCH_3})$ 0.45 ppm, $J(\mathrm{CH_3C{=}CH}) \sim 0.8$, $J\left({=}\mathrm{C}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\end{smallmatrix}\right) \sim 0.3$ Hz.

The *O*-isomer content of the reaction mixture gradually decreased to 4% after one or two days at room temperature and then remained constant. It seems likely that the mixture containing 4% of *O*-isomer and 96% of *C*-isomer is in equilibrium; n_D^{20} 1.4438, d_4^{20} 1.1372. (Found: C, 41.84; H, 8.25; Ge, 41.87. $\mathrm{C_6H_{14}GeO}$ calcd.: C, 41.23; H, 8.07; Ge, 41.54%).

The position of this equilibrium depends largely on the temperature. On heating, the *O*-isomer content of the mixture increases, and at 170° (heating in the ampoule of the NMR spectrometer) is 17%; on cooling to room temperature it decreases to 4% again. Rectification of the equilibrium mixture of *O*- and *C*-isomers on a column with 7TP, enables trimethylisopropenyloxygermane (*O*-isomer) to be isolated, the amount of the latter in the distillate being much higher than in the initial equilibrium mixture. On standing, the *O*-isomer slowly isomerises to trimethylgermylacetone (*C*-isomer). In the presence of catalytic amounts of trimethylbromogermane, the process is considerably accelerated.

The data obtained suggest that in the trimethylgermylacetone–trimethylisopropenyloxygermane system there is an equilibrium between the isomers (germanotropy) which can be shifted by various means.

$$Me_3GeCH_2COCH_3 \rightleftarrows Me_3GeOC(CH_3){=}CH_2$$

Previously it was found* that in the presence of catalytic amounts of certain reagents, or simply on heating**, relatively unstable organosilicon derivatives of keto-enolic systems rearrange to more thermodynamically stable compounds, *e.g.* β-silyl ketones to *O*-silyl-substituted enols, and *O*-silyl-*O*-methylketene acetals to esters of silylated acetic acid. The equilibrium of the reactions discussed is practically entirely shifted towards the formation of the more stable isomer. As a result, the interaction of α-metalated carbonyl compounds with halosilanes under thermodynamically controlled conditions (using reagents catalysing rearrangements—specially added or formed as intermediates—prolonged heating of the reaction mixture) gives rise to the formation of only one isomer of the two probable silylation products.

The data presented on the reaction of trimethylbromogermane with tripropylstannylacetone, and the results on the interactions of other halogermanes with α-metalated aldehydes and ketones suggest that thermodynamically controlled germylation leads to the formation of an equilibrium isomeric mixture, while thermodynamically controlled silylation yields only one, more thermodynamically, stable isomer. The methods for shifting the equilibrium in question will be discussed in a further communication.

REFERENCES

1 I. F. Lutsenko, Yu. Baukov, O. V. Dudukina and E. N. Kramarova, *J. Organometal. Chem.*, 11 (1968) 35.
2 A. G. Brook, D. M. MacRae and W. W. Limburg, *J. Amer. Chem. Soc.*, 89 (1967) 5493.

---

* See, for example, ref. 1 and literature cited there.

** For thermic isomerisation of β-silyl ketones into *O*-silyl-substituted enols see also ref. 2.