Chemistry

1964

SovietRxiv

Abstract

Full Text

Chemistry

Yu. I. Baukov, G. S. Burlachenko, I. F. Lutsenko

On the Rearrangement of α-Trialkylsiloxyvinyl Alkyl Ethers into Esters of Trialkylsilylacetic Acid

(Presented by Academician A. N. Nesmeyanov, January 9, 1964)

A broad study of the reactivity of α-mercurated oxo compounds has shown that this interesting class of organomercury derivatives is capable of exhibiting dual reactivity: reacting without transfer of the reaction center (formation of products of reaction at C) and with transfer of the reaction center (formation of products of reaction at the oxygen atom of the carbonyl group) (^{1}). Methods developed in recent years for the synthesis of esters of α-metalated carboxylic acids (^{2}), which have made them readily accessible, have made it possible to study their behavior in various reactions and to find new examples of the dual reactivity of organometallic compounds.

The present article presents the results of an investigation of the reaction of esters of mercurated acetic acid with trialkyliodosilanes and the conditions of a new rearrangement, found by us, in the series of organosilicon compounds.

Trialkyliodosilanes readily react with esters of α-mercurated carboxylic acids. By changing the ratio of the reagents, the reaction can be carried either to the ester of an α-iodomercuricarboxylic acid or to mercuric iodide. Further study showed that, depending on the structure of the starting compounds and the conditions under which the reaction is carried out, two types of products may be formed: esters of α-silylated carboxylic acids (reaction without transfer of the reaction center), or α-trialkylsiloxyvinyl alkyl ethers (reaction with transfer of the reaction center).

When the reaction between triethyliodosilane and the methyl ester of mercuriacetic acid is carried out in benzene or carbon tetrachloride, α-triethylsiloxyvinyl methyl ether is formed in a yield of about 50%. The use of dichloroethane or chloroform as solvents leads to formation only of the methyl ester of triethylsilylacetic acid (yield about 60%).

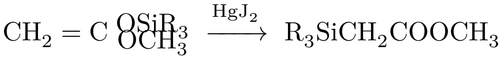
$$R_3SiJ \xrightarrow[-JHgCH_2COOCH_3]{Hg(CH_2COOCH_3)_2} \begin{cases} \xrightarrow[CCl_4]{\text{benzene}} CH_2=C(OCH_3)OSiR_3 \xrightarrow{LiAlH_4} R_3SiH \\ \xrightarrow[CHCl_3]{\text{dichloroethane}} R_3SiCH_2COOCH_3 \xrightarrow{LiAlH_4} R_3SiCH_2CH_2OH \end{cases}$$

The isomeric compounds obtained proved to differ substantially in their constants and in their IR and Raman spectra. In the case of esters of silylated acetic acid (reaction at C), frequencies characteristic of the ester group were found in the spectra. In the products of reaction with transfer of the reaction center (reaction at O), frequencies corresponding to a carbon-carbon double bond were found.

The structure of the isolated products was also confirmed by chemical reactions. Thus, α-triethylsiloxyvinyl methyl ether is readily hydrolyzed by water, giving methyl acetate and triethylsilanol; the methyl ester of triethylsilylacetic acid is unchanged under these conditions. On reduction with $LiAlH_4$ of the products of reaction at O (α-siloxyvinyl ethers), the corresponding trialkylsilanes were isolated; the products of reaction at C (esters p. 119

silylated acetic acid) are reduced by $LiAlH_4$ without cleavage of the Si—C bond to the corresponding alcohols $R_3SiCH_2CH_2OH$, analogously to what we found for esters of trialkylgermylacetic acid (^{3}).

It has also been established that, under certain conditions, O-derivatives can be converted into the C-derivatives isomeric with them. This rearrangement proceeds best when α-siloxyvinyl ethers are heated for several hours at 70° in the presence of mercuric iodide (5-7 mol.%)



$$CH_2=C\begin{matrix}OSiR_3\\OCH_3\end{matrix} \xrightarrow{HgJ_2} R_3SiCH_2COOCH_3$$

The conversion into the C-form is judged from the change in the constants of the compound, the data of the IR spectrum, and the reduction products.

The fact of rearrangement of O-silylation products into C-silylation products makes an essential addition to the scheme for the formation of final products in reactions of compounds exhibiting dual reactivity, since in some cases it permits the assumption that the formation of one of the isomeric forms may occur as a result of rearrangement of the other form initially produced and, consequently, depends on their relative stability.

At present we are carrying out a further study of the conditions for the formation of O- and C-derivatives as a function of the structure of the iodosilane and of the organomercury compound, as well as of the mechanism of the rearrangement discovered.

Experimental Part

α-Triethylsiloxyvinyl methyl ether. To a solution of 69.3 g of the methyl ester of mercuric acetic acid in 300 ml of anhydrous benzene, a solution of 43.5 g of triethyliodosilane in 30 ml of benzene is added dropwise with stirring. Then 500 ml of petroleum ether is poured in and the reaction mixture is cooled to $-30°$. The precipitate that separates is filtered off, washed with petroleum ether, and recrystallized from benzene to give 72 g of the methyl ester of iodomercuriacetic acid (yield 90%), m.p. 107-108°. The solvent is distilled off from the filtrate, and from the residue, by vacuum distillation, 17.7 g of α-triethylsiloxyvinyl methyl ether is isolated. Yield 53%, b.p. 65-66.5°/7 mm, n_D^{20} 1.4355, d_4^{20} 0.8870, MR_D 55.45; calculated 55.56.

Found, %: C 57.24; H 10.80; Si 15.13.
$C_9H_{20}SiO_2$. Calculated, %: C 57.40; H 10.71; Si 14.90.

In the IR spectrum of the compound obtained, an intense absorption band with frequency 1652 cm^{-1} was found; in the Raman spectrum, a frequency 1658 sh (J vis. 12), corresponding to vibrations of the $C = C$ bond.

Methyl ester of triethylsilylacetic acid. To a solution of 22.8 g of the methyl ester of mercuric acetic acid in 50 ml of dichloroethane, a solution of 14.6 g of triethyliodosilane in 10 ml of dichloroethane is added dropwise. The subsequent work-up of the reaction mixture is carried out analogously to that described above. Distillation gives 6.8 g of the methyl ester of triethylsilylacetic acid. Yield 60%, b.p. 75-77°/7 mm, n_D^{20} 1.4399, d_4^{20} 0.9019, MR_D 55.02; calculated 55.18.

Found, %: C 57.70; H 10.94; Si 15.30.
$C_9H_{20}SiO_2$. Calculated, %: C 57.40; H 10.71; Si 14.90.

In the IR spectrum of the compound obtained, an intense absorption band with frequency 1732 cm^{-1} was found; in the Raman spectrum, a frequency 1734 diff. (J vis. 2.5), corresponding to vibrations of the ester group.

Rearrangement of α-triethylsiloxyvinyl methyl ether into methyl triethylsilylacetate. 7 g of α-triethylsiloxyvinyl methyl ether and 1 g of mercuric iodide are stirred for half an hour with cooling by cold water and then for another hour at 70°. The mixture is decanted from the mercuric iodide; upon distillation of the organic portion, 5.8 g (83%) of methyl triethylsilylacetate is obtained, b.p. 79–82°/8 mm, n_D^{20} 1.4412, d_4^{20} 0.9030; MR_D 55.08; calculated 55.18.

In the IR spectrum of the compound obtained, an intense absorption band was found in the region of 1730 cm^{-1}, corresponding to vibrations of the ester group; reduction with $LiAlH_4$ leads to the formation of 2-hydroxyethyltriethylsilane in 78% yield.

Moscow State University
named after M. V. Lomonosov

Received
8 I 1964

CITED LITERATURE

1. A. N. Nesmeyanov, I. F. Lutsenko, Z. M. Tumanova, *Izv. AN SSSR, OKhN*, 1949, 601; *Uch. zap. Moskovsk. univ.*, **132**, 44 (1950).

2. I. F. Lutsenko, V. L. Foss, N. L. Ivanova, *DAN*, **141**, No. 1107 (1961); I. F. Lutsenko, S. V. Ponomarev, *ZhOKh*, **31**, 2025 (1961); V. L. Foss, M. A. Zhadina, I. F. Lutsenko, A. N. Nesmeyanov, *ZhOKh*, **33**, 1927 (1963).

3. I. F. Lutsenko, Yu. I. Baukov, B. N. Khasapov, *ZhOKh*, **33**, 2724 (1963).

Note: Figure translations are in progress. See original paper for figures.