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REACTION OF COMBINATION OF TRIMETHYLVINYLSILANE WITH ORGANIC HALIDES CATALYZED BY PALLADIUM DERIVATIVES

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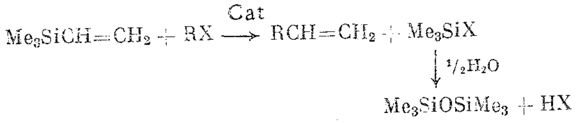
The reactions of cleavage of the Si—C bonds by the action of transition metal complexes open up new paths for using organosilicon compounds in organic synthesis and catalysis [1]. Recently, research workers have paid great attention to the vinylation reactions of organic halides by means of organometallic compounds, catalyzed by transition metal complexes [2-4]. Interest in the synthesis of vinyl compounds is due to their wide use in practice.

In the present work, we carried out the vinylation of halides of the benzene, naphthalene, pyridine, and carborane series by reaction with trimethylvinylsilane in the presence of catalytic amounts of Pd complexes at 100°C in DMFA or in hexametapol (HMPT).



$$\begin{tikzcd} Me_3SiCH{=}CH_2 + RX \arrow[r, "Cat"] & RCH{=}CH_2 + Me_3SiX \arrow[d, "{}^1/_2H_2O"] \\ & Me_3SiOSiMe_3 + HX \end{tikzcd}$$

Table 1 shows that, in the case of halo-derivatives of pyridine, the bromide is more active than the iodide, while for halides of the naphthalene series, the opposite is observed.

The vinylation reaction is catalyzed not only by bis-π-allylpalladium chloride, but also by a wide range of Pd(II) and Pd(0) derivatives: $LiPdCl_3$, $(PhCN)_2PdCl_2$, $(MeCN)_2PdCl_2$, $(Ph_3P)_4 \cdot Pd$, Pd/C. According to their activity in the vinylation reaction, the Pd complexes can be arranged in the following sequence:*

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*The yields of styrene at 100°C after 5 h are given in brackets.

TABLE 1. Reactions of Combination of $Me_3SiCH{=}CH_2$ with RX Catalyzed by $(\pi\text{-}C_3H_5PdCl)_2$ (DMFA, 100°, 5 h, molar ratio silane: RX:catalyst = 2:1:0.1)

RX	Yield of $RCH = CH_2$, % based on RX	RX	Yield of $RCH = CH_2$, % based on RX
α-Iodonaphthalene	55	Iodobenzene	35
α-Bromonaphthalene	2	Iodobenzene	53 *
9-Iodo-m-carborane	4	p-Ethoxyiodobenzene	14
α-Bromopyridine	30	p-Nitroiodobenzene	10
α-Iodopyridine	23	p,p'-Diiodobenzene	5

*In the presence of Et_3N, after 15 h.

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$$\underset{(35)}{(\pi\text{-}C_3H_5PdCl)_2} > \underset{(20)}{LiPdCl_3} > \underset{(11)}{(PhCN)_2PdCl_2} = \underset{(11)}{(MeCN)_2PdCl_2} > \underset{(6)}{(Ph_3P)_4Pd} > \underset{(3)}{Pd/C}$$

Here, as in the cross-combination of organotin compounds with organic halide derivatives, bis-π-allylpalladium chloride has the highest activity [4].

The influence of the addition of Et_3N base to the reaction mixture (in equimolar amounts with respect to RX) is not completely clear-cut. In the case of pyridine derivatives, Et_3N inhibits the process, while in the reaction with halides of the benzene series, in some cases the amine somewhat activates the reaction (in its presence the yield of styrene increases 1.3 times).

At the conclusion of the present investigation, a paper appeared on the use of trimethylvinylsilane for vinylation of aryl halides of the benzene series catalyzed by palladium acetate and palladium on carbon [5].

The vinylation reaction of organic halogen derivatives by organosilicon compounds have advantages over similar reactions using organometallic compounds (Li, Mg, Hg, Sn, etc.) because of the chemical stability, nontoxicity, and also relative availability of organic silicon derivatives.

EXPERIMENTAL

Reaction of α-Iodonaphthalene with $Me_3SiCH{=}CH_2$. A mixture of 0.04 g (0.4 mmole) of $Me_3 \cdot SiCH{=}CH_2$, 0.04 g (0.3 mmole) of $C_{10}H_7I$, 0.007 g (0.02 mole) of $(\pi\text{-}C_3H_5PdCl)_2$, 0.01 g of tetraline (internal standard) in 1 ml of DMFA containing 0.7% of water was heated in an ampul for 5 h at 100°C. Analysis of the gases showed the presence of ethylene, propylene, and a small amount of divinyl in the products. The reaction mixture was treated with 1 ml of H_2O, and the aqueous layer was extracted by pentane. The pentane extracts were dried over anhydrous $MgSO_4$. After distillation of the solvent, 0.017 g (55%) of vinylnaphthalene were detected. The reactions with all other halogen derivatives were carried out similarly. The reaction with $(Ph_3P)_4Pd$ was carried out in argon.

Styrene was determined on the LKhM-8MD chromatograph with a heat conductivity detector on a column with 12% PEGA, 5 m × 3 mm, 120°C. Vinylpyridine was determined on a column with Tween-20, 3 m × 3 mm, 150°C. Two gases from the reaction mixture were identified on the Gasochrom 3101 chromatograph, on a column with 15% dimethylsulfolane on NAW Chromatone, 7 m. The substituted styrenes, vinylnaphthalene, and vinylcarborane were determined on the Biochrom chromatograph, using a capillary column with a XE-60 phase, and chromato-mass spectrometrically on the Varian MAT CH-8 apparatus with DS-200 column.

There were the corresponding peaks of the molecular ions in the mass spectra for all the products obtained: vinylnaphthalene — 154, vinylcarborane — 170, and the corresponding isotopic peaks p-nitrostyrene — 149, p-ethoxystyrene — 148, p-isodostyrene — 230. Dissociation with elimination of ethylene and acetylene confirms the presence of the vinyl group in the compounds. The character of the fragmentation corresponded, in general, to the literature data for these classes of compounds [6].

We wish to express our gratitude to E. I. Mysov for taking the chromato-mass spectra.

CONCLUSIONS

It has been discovered that halopyridines, halonaphthalene, iodocarborane, and aryl iodides are vinylated by a reaction of trimethylvinylsilane, catalyzed by palladium complexes.

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