

LETTERS
TO THE EDITOR

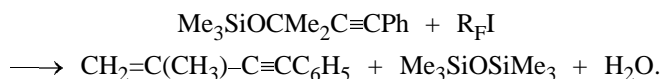
Unusual Desilanalysis
of 1,1-Dimethyl-1-(trimethylsiloxy)-3-phenylpropyne

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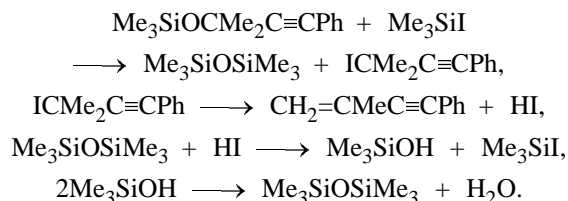
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Proceeding with our studies on homolytic addition to group 14 unsaturated derivatives [1, 2] we tried to effect a photoinduced reaction of polyhaloalkanes with trimethylsilyl ethers of phenylethynylcarbinols of the general formula $\text{Me}_3\text{SiORR}^1\text{CC}\equiv\text{CPh}$, where $\text{R} = \text{R}^1 = \text{H}$ (**I**); $\text{R} = \text{H}$, $\text{R}^1 = \text{Me}$ (**II**); and $\text{R} = \text{R}^1 = \text{Me}$ (**III**). On UV irradiation of equimolar mixtures of bromotrichloromethane or heptafluoroiodopropane with compounds **I** or **II** we observed no reaction within 50 h. This is evidently explained by steric shielding of the triple bond, preventing attack of the polyhaloalkyl radical. It was unexpectedly found that irradiation of a mixture of heptafluoroiodopropane or trifluoroiodomethane with ether **III** results in cleavage of trimethylsilanol to give 2-methyl-4-phenylbut-1-en-3-yne (**IV**). At the same time, the starting polyhaloalkane remains practically unchanged.



This reaction is similar to the classical dehydration of tertiary acetylenic alcohols under the action of sulfuric acid, discovered by Favorskii [3, 4].

We propose that on UV irradiation of a mixture of the starting compounds, a small amount of iodotrimethylsilane is formed, which induces the above-mentioned reactions. This proposal is confirmed by the fact that in the presence of catalytic amounts of iodotrimethylsilane compound **III** converts to **IV** within several hours at room temperature.



Reaction of ether III with heptafluoroiodopropane. A mixture of 23.2 g of **III** and 26.9 g of hepta-

fluoroiodopropane in a sealed ampule was subjected to UV irradiation for 50 h. Distillation of the reaction mixture gave the starting heptafluoroiodopropane (almost quantitative recovery) and 18.3 g (78%) of 2-methyl-4-phenylbut-1-en-3-yne (**IV**). bp 88°C (3 mm), n_{D}^{20} 1.5742 {published data [5]: bp 87–88°C (7 mm), n_{D}^{20} 1.5750}. ^1H NMR spectrum (CDCl_3), δ , ppm: 7.29 m (5H, C_6H_5); 5.36 d.q (1H, *cis*-HC=); 5.26 d.q (1H, *trans*-HC=); 1.96 d.d [3H, CH_3 , *cis*- $\text{J}(\text{CH}_3\text{C}=\text{CH})$ 1.0 Hz, *trans*- $\text{J}(\text{CH}_3\text{C}=\text{CH})$ 1.6 Hz).

Reaction of ether III with iodotrimethylsilane.

A mixture of **III** and several drops of iodotrimethylsilane was placed in a two-necked flask equipped with a reflux condenser with a calcium chloride tube and a mechanical stirrer. After 2-h stirring, according to GLC data, the starting compound almost completely converted to 2-methyl-4-phenylbut-1-en-3-yne (**IV**). The product was isolated by vacuum distillation in 89% yield.

The ^1H NMR spectrum was recorded on a Bruker DPX-400 spectrometer in CDCl_3 against internal TMS. Gas chromatography was carried out on a Tsvet-500 chromatograph, detector katharometer, glass column (3000×4 mm), packing 10% of PMS-1000 on InertonSuper (0.120–0.150 mm).

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