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LETTERS TO THE EDITOR

Unusual Product of the Si–C Bond Cleavage in Diallyldiphenylsilane

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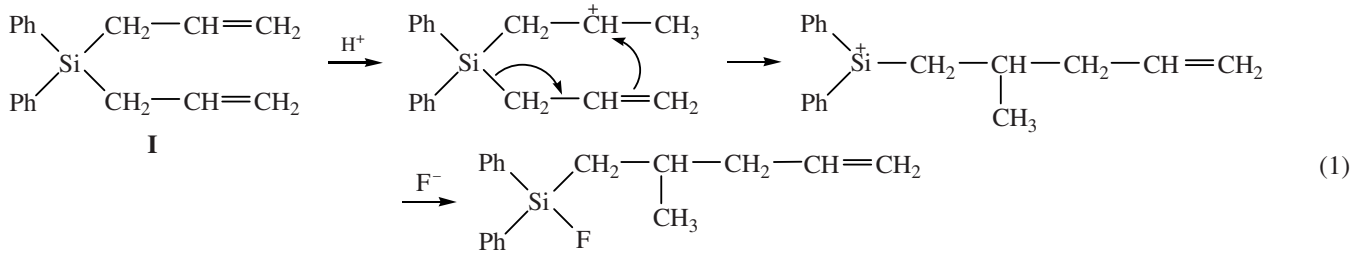
In continuation of the studies of thiasilacycloalkanes [1–5] and aiming at a synthesis of SiF-containing heterocycles, we have investigated the reaction of diallyldiphenylsilane (**I**) with complex $BF_3 \cdot 2AcOH$ (**II**). Complex **II** is used as an efficient and selective reagent for splitting the Si–Ph bond in $–SiR_2Ph$ and $–SiRPh_2$ groups to afford $–SiFR_2$ and $–SiF_2R$ derivatives [6–8]. Therefore, we planned to prepare diallyldifluorosilane and to use it for further cyclization. However, neither the target diallyldifluorosilane nor its precursor, diallyl(fluoro)phenylsilane, are formed in the reaction of silane **I** with complex **II**. Instead, the cleavage of one of the Si–C_{sp3} bonds occurs with the formation of fluoro(2-methyl-4-pentenyl)diphenylsilane **III**. The structure of product **III** is proved by ^1H, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopy including homo- and heteronuclear spectra COSY and HSQC(^{13}C–H).

Such a course of the reaction, which is distinct from the known Si–Ph bond splitting under the action of $BF_3 \cdot 2AcOH$ [6-8], is due to the presence of two allyl groups in the molecule of silane **II**. The carbocation that is formed by protonation of the allyl group [9] interacts with the π-bond of the second allyl group resulting in the cleavage of the Si–C_{sp3} bond by the mechanism of the intramolecular $S_{E'}$ allylic substitution and addition of the fluoride ion to the silyl cation formed.



I **III** (1)

Easier cleavage of the Si–All bond as compared to the Si–Ph bond is consistent with the data on splitting of different Si–C bonds under the action of CF_3SO_3H [10]. However, the presence of two allyl groups at the silicon atom is not in itself a sufficient condition for rearrangement (1) to occur. Thus, under the action of CF_3SO_3H diallyl(methyl)vinylsilane eliminates in succession two molecules of propene to give CH_2=CHSi(Me)$(OSO_2CF_3)_2$ [10]. We believe that it is due to deactivation of the π-bond of the second allyl group in the intermediate carbocation in strongly acidic medium.

Fluoro(2-methyl-4-pentenyl)diphenylsilane. To a solution of 0.475 g of diallyldiphenylsilane (**I**) in 3 ml of dry CH_2Cl_2 0.338 g of complex $BF_3 \cdot 2AcOH$ (**II**) in

2 ml of CH_2Cl_2 was added dropwise. The reaction mixture was refluxed for 4 h, washed with cold water (2.30 ml), dried over $CaCl_2$, filtered, and the solvent was removed under vacuum. 0.316 g (63%) of fluoro (2-methyl-4-pentenyl)diphenylsilane (**III**) was obtained and purified by column chromatography on silica gel 60 (Merck), elution with hexane and hexane–ether mixtures from 20:1 to 5:1. IR spectrum, ν, cm^{-1}: 3080, 2955, 1640, 1590, 1420, 1105, 830, 700. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.97 d (3H, CH_3, J 6.7 Hz), 1.13 d.d.d (1H, $SiCH^A$, J_{HH} 15.4, 6.9, J_{HF} 8.7 Hz), 1.39 d.d.d (1H, $SiCH^B$, J_{HH} 4.86, J_{HF} 10.0 Hz), 1.90 m (1H, CH), 2.02 d. t (1H, CH^AC=, J 13.3, 6.9 Hz), 2.10 d.t (1H, CH^BC=, J 6.4 Hz), 4.95 d (1H, =CH-*trans*, J 17.2 Hz), 5.01 d (1H, =CH-*cis*, J 10.2 Hz), 5.74 d.d.t (1H, CH=, J 17.2, 10.2, 7.2 Hz), 7.43 m (6H, $H_{m,p}$), 7.62 m (4H, H_o). ^{13}C NMR spectrum, δ, ppm: 21.86 d ($SiCH_2$, J_{CF} 13.6 Hz), 22.51 d (CH_3, J_{CF} 1.1 Hz), 28.51 s (*C*HMe), 44.50 d (CH_2C=C, J_{CF} 1.1 Hz), 116.23 s (=CH_2), 128.03 d (C_m, J_{CF} 2.2 Hz), 130.44 s (C_n), 133.85 d (C^I, J_{CF} 16.5 Hz), 133.99 d (C_o, J_{CF} 2.2 Hz), 134.03 d (C_o', J_{CF} 2.2 Hz), 134.20 d ($C^{1'}$, J_{CF} 16.1 Hz), 137.04 s (CH=). ^{19}F NMR, δ, ppm: –169.80 m (J_{SiF} 286.5 Hz). ^{29}Si NMR, δ, ppm: 6.35 d (J_{SiF} 286.7 Hz). Found, %: C 76.17; H 7.32; F 6.81; Si 9.89. $C_8H_{21}FSi$. Calculated, %: C 76.01; H 7.44; F 6.68; Si 9.87.

IR spectrum was taken on a Specord IR-75 instrument from thin layer, NMR spectra were recorded on a Bruker DPX400 spectrometer at 400 (^1H), 100 (^{13}C), 376 (^{19}F), and 80 MHz (^{29}Si) from solutions in $CDCl_3$, chemical shifts are given with respect to TMS (^1H, ^{13}C, ^{29}Si) and CCl_3F (^{19}F).

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