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LETTERS TO THE EDITOR

Synthesis of Phenylsilane Doubly Tritium-labeled in the Benzene Ring

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Over many years we have performed a research into ion-molecular reactions of carbenium and silicenium ions [1–3] generated by the nuclear chemical technique [4]. This technique has some unique features, one of which is the possibility of generating cations with a strictly fixed charge localization defined exclusively by the position of tritium in the source of the cations. To generate free cations by the nuclear chemical technique, one should first synthesize to a source of these cations. We have synthesized phenylsilane tritium-labeled in the *ortho* and *para* positions of the benzene ring to use it as a source of silyl-substituted phenyl cations. The synthesis of tritium-labeled phenylsilane I was based on catalytic exchange of tritium for halogen in (2,4-dibromophenyl)trimethoxysilane (II) followed by reduction of methoxy derivative III with lithium aluminum hydride [5]. The use of trimethoxy derivative II instead of (2,4-dibromophenyl)silane as the starting material was motivated by the necessity to avoid replacement of the Si–H hydrogen by tritium as a result of the possible catalytic isotope exchange.

(2,4-Dibromophenyl)trimethoxysilane (II) was prepared by the catalytic bromination of phenyltrichlorosilane (IV) with molecular bromine by the procedure [6]. Further (2,4-dibromophenyl)ttichlorosilane (V) was subjected to methanolysis by a modified procedure [7].

$$\begin{array}{c} \mbox{PhSiCl}_3 \xrightarrow{Br_2, Fe} 2,4-Br_2C_6H_3SiCl_3 \xrightarrow{MeOH, Et_3N} 2,4-Br_2C_6H_3Si(OMe)_3, \\ \mbox{IV} V V & II \\ \mbox{II} \xrightarrow{2T_2, Pd/BaSO_4, Et_3N} 2,4-T_2C_6H_3Si(OMe)_3, \\ \mbox{III} \xrightarrow{Et_2O, -TBr} & III \\ \mbox{III} \xrightarrow{LiAlH_4} 2,4-T_2C_6H_3SiH_3. \\ \mbox{II} \xrightarrow{LiAlH_4} III \xrightarrow{LiAlH$$

The structure and purity of the resulting compounds were determined by means of NMR and IR spectroscopy and GLC.

2,4-Ditritiophenylsilane (I). A 2-ml ampule was charged with 5–10 mg of catalyst (5% Pd on barium sulfate) that was activated at 160°C for 1 h in a vacuum (10^{-3} mm) . Ethereal solution (200 µl) of 1.4 µl of dibromo derivative II and 2.2 µl of triethyal-amine was then added. The ampule was cooled with

liquid nitrogen, evaculated, filled with molecular tritium to 200 mm Hg, and sealed. The reaction was performed at room temperature under vigorous stirring. Reaction time 2 h. Unreacted tritium was removed in a vacuum. The residual solution of labeled phenyltrimethoxysilane **III** was transferred into a tube containing 0.2 ml of ethereal solution of 0.3 mg of lithium aluminum hydride and 0.06 mg of aluminum bromide. The reaction was complete within a few minutes, after which the tube was evacuated, the ether was removed

at -70° C, and labeled phenylsilane I was collected into a receiver cooled with liquid nitrogen. Phenylsilane I was diluted with 1 ml of hexane, and the concentration of the solution was determined by GLC. The yield of compound I was 20–25% (per gaseous tritium). The activity of an aliquot was measured in a fluid-scintillation counter and quantified by the internal calibration technique. The calculated specific activity of the sample was 50 Ci/mmol, which corresponds to a 1.8 label multiplicity in the benzene ring.

The concentration of phenylsilane **I** was determined by GLC on a Tsvet-500 chromatograph (thermal conductivity detector, column 2000×2 mm, packing 5% Silicone SE-30 on Inerton-AW, carrier gas helium). Activity measurements were performed on a Beta-2 fluid analyzer (ZhS-8 scintillator), internal reference labeled benzene.

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