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SYNTHESIS OF n-OCTYLTRICHLOROSILANE LABELED WITH ^{13}C IN THE TERMINAL POSITION

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SUMMARY

This report describes the synthesis of carbon-13 labeled n-octyltrichlorosilane from ^{13}C-barium carbonate. The product is labeled at the 8-position of the alkyl chain.

Key Words: n-octyltrichlorosilane, ^{13}C-labeled alkyltrichlorosilanes, reagents for labeling chromatographic surfaces, surface modification reagents.

INTRODUCTION

Although the importance of alkylchlorosilanes as surface modifying reagents is well established, the nature of the surface once modified continues to be debated. This is especially true for chromatographic surfaces. Questions of surface solvation and topography are keys to understanding solute-surface interaction and hence retention in liquid chromotography (LC). The potential of using carbon magnetic resonance (CMR) to study alkyl modified LC materials has been discussed (1). Currently carbon-13 NMR studies of adsorbed and bonded molecules on silica surfaces is receiving some attention (2-9). All of these studies have been run under conditions quite different from the actual solvent environment present in a liquid chromatographic column.

The feasibility of using a combination of both LC and NMR experiments to generate new information about alkyl modified surfaces in mixed mobile phase systems has been demonstrated (10). Initial CMR studies have shown

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significant differences in line shape depending on the solvent. Studies were carried out on a n-heptyl terminal labeled material. The synthesis of the n-heptyltrichlorosilane monomer was reported previously (1). The product was prepared in a 24% yield at the 7-position using ^{13}C-methyl iodide.

The current procedure describes the preparation of n-octyltrichlorosilane using ^{13}C-barium carbonate. The product has been labeled at the 8 position of the alkyl chain. The current procedure has the advantage of savings in cost due to higher yields and a cheaper ^{13}C starting material. Additionally, the method is a more generalized procedure and is potentially useful for preparing various n-terminal silane monomers.

EXPERIMENTAL

Octanoic -^{13}C Acid

Heptenylmagnesium bromide, which was prepared from 0.10 mole of heptenylbromide and 0.12 mole of magnesium turnings in 150 ml of ether, was allowed to react with 0.05 mole of carbon dioxide at a temperature maintained with dry ice and acetone. The carbon dioxide was generated from a mixture of 0.012 mole of labeled ^{13}C-barium carbonate and 0.038 mole of unlabeled barium carbonate using the technique described by Dauben, et al. (11). After completing the above steps, the magnesium salts were decomposed with 2M HCl. The resulting product was extracted into ether and the ether solution was washed with water and then with 5% sodium hydroxide. The sodium hydroxide layer which contained the material of interest was acidified. The product was re-extracted into ether. This solution was dried over anhydrous sodium sulfate, filtered and evaporated to dryness. A yield of 0.035 mole (70%) of acid was obtained.

Octenol-^{13}C

The 0.035 mole of octenoic-^{13}C acid was reduced with lithium aluminum hydride according to the procedure reported by Heusler, et al. (12) to yield 0.029 mole (83%) of Octenol-^{13}C.

Octenyl p-toluenesulfonate-^{13}C

The 0.029 mole of the above alcohol was mixed with 10ml of dry pyridine and cooled to 0°C. Then 6g of p-toluenesulfonylchloride were added and the solution stored for four hours at 0°C. The mixture was diluted with 40ml of 3M hydrochloric acid and extracted with ether. The ether layer was washed with both 3M hydrochloric acid and water and dried over anhydrous sodium sulfate. The filtered ether layer was removed under reduced pressure to yield 0.023 mole (79%) of the tosylate.

Octene-^{13}C

The 0.023 mole of the labeled tosylate was reacted with 0.046 mole of lithium triethylborohydride. The procedure employed was similar to that reported by Brown, et al. (13) for cyclooctyltosylate. The yield of octene was 0.019 mole (83%).

Octyltrichlorosilane-^{13}C

The 0.019 mole of octene was reacted with 0.04 mole of trichlorosilane using the procedure reported previously (1). The yield of octyltrichlorosilane was 0.010 mole (53%).

RESULTS AND DISCUSSIONS

The synthesis scheme that was employed is summarized in the following reaction sequence.

$$CH_2{=}CH(CH_2)_5Br \xrightarrow[\text{Ether}]{\text{Mg}} CH_2{=}CH(CH_2)_5\text{-}MgBr \xrightarrow{{}^*CO_2}$$

$$CH_2{=}CH\text{-}(CH_2)_5{}^*CO_2H \xrightarrow[\text{Ether}]{LiAlH_4} CH_2{=}CH\text{-}(CH_2)_5\text{-}{}^*CH_2\text{-}OH \xrightarrow[\text{Pyridine}]{\text{TsCl}}$$

$$CH_2{=}CH\ (CH_2)_5\text{-}{}^*CH_2OTS \xrightarrow[\text{THF}]{LiB(C_2H_5)_3H} CH_2{=}CH(CH_2)_5\text{-}{}^*CH_3 \xrightarrow[H_2PtCl_6]{HSiCl_3}$$

$$Cl_3SiCH_2\text{-}CH_2(CH_2)_5 \text{—}{}^*CH_3$$

The overall n-octyltrichlorosilane-8-^{13}C was produced in a 20% yield from barium carbonate. All intermediate reaction products were characterized by IR spectroscopy. The final product, n-octyltrichlorosilane-^{13}C was examined by IR and carbon-13 NMR techniques.

Carbon-13 spectra of the enriched final product and commercially available n-octyltrichlorosilane were obtained under identical experimental conditions using a Varian Model FT-80 spectrometer. In both cases within experimental error each of the observed corresponding NMR lines were identical in chemical shift. Both spectra contained six lines instead of eight due to overlap of some resonances. These shift results along with peak intensity data are summarized in the following table.

Labeled Material		Unlabeled Material*	
Chemical shift** ppm	Intensity	Chemical Shift** ppm	Intensity
14.09	200	14.09	32
22.32	14	22.41	64
22.66	12	22.75	50
24.40	13	24.51	55
29.07	19	29.14	96
31.89	24	31.97	100

*Obtained from Petrarch Systems„ Inc.
**Referenced to TMS

Using the method reported by Wright, et al. (14) the calculated percentage enrichment for the labeled product was 26%. This result is in good agreement with a theoretical value of 24% calculated from the ratio of labeled to unlabeled barium carbonate used as starting material.

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