

SYNTHESIS OF n-HEPTYLTRICHLOROSILANE 7-¹³C FOR PREPARATION OF LABELED CHROMATOGRAPHIC SURFACES

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SUMMARY

This report describes the synthesis of carbon-13 labeled n-heptyltrichlorosilane from ¹³C methyl iodide. The product is labeled at the 7-position of the alkyl chain in a 24% yield.

Key Words: n-heptyltrichlorosilane, ¹³C labeled alkyltrichlorosilanes, reagents for labeling chromatographic surfaces, surface modification reagents

INTRODUCTION

Alkyltrichlorosilanes have been and continue to be important as surface modification reagents. Of particular interest have been the preparation of various bonded layers for use as chromatographic column materials. Most of these materials have been employed in the reversed-phase mode. Although many non-polar surfaces could be utilized as reversed-phase packings, the linear alkanes typically have been the attached surface groups of choice. Reversed-phase separations on these non-polar surfaces are carried out using polar mobile phases which are commonly combinations of either water and acetonitrile, or water and methanol.

Over the past decade the nature of reversed-phase interaction has been a topic of considerable interest as well as controversy. Various models of the hydrophobic surface have ranged from a rigid to a folded orientation (1). Recently, a more dynamic description of the surface has been suggested (2). In this description the surface groups may assume different orientational and

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solvated states depending on various physical operating parameters. Up to now most of the descriptive arguments have been based on chromatographic data. The related non-chromatographic data which have been collected usually have been generated from either techniques which measure bulk properties of the adsorbent or have been measured in a solvated or non-solvated condition quite different from the condition which exists in chromatographic columns.

Of the analytical techniques available, NMR seems to be the method of choice since the solvent environment can be made to mimic closely that of a liquid chromatographic experiment. However since chromatographic supports contain low levels of attached groups (typically 5 to 15% w/w) coupled with the low relative natural abundance of the ^{13}C nuclei, collection times for a single NMR experiment become prohibitively long. Thus labeling of a specific carbon maximize data collection efficiency. Additionally, since surface attached carbons may produce broad line spectra, labeling eliminates interferences from other carbons.

Based on previous chromatographic results (2), a labeled heptyl group was selected for initial NMR investigations of molecular motion as a function of solvent and other related conditions. The preparation of such a terminally labeled monomer is described. It is reasonable to suggest that this same scheme with some modifications or change in initial starting materials can be used to prepare a number of different alkyltrichlorosilane monomers.

EXPERIMENTAL

Tetrahydropyran-2-methyl chloride

Tetrahydropyran-2-methyl chloride was prepared from tetrahydropyran-2-methanol by the procedure of Kirner (3) for the conversion of tetrahydrofurfuryl alcohol to its chloride. All reported conditions were followed without modification. The product which was obtained in 50% yield boiled at 35-37°C at 1mm pressure.

6-Hexenol

Tetrahydropyran-2-methyl chloride initially was reacted with sodium and

subsequently hydrolyzed to the resulting 6-hexenol. The procedure employed was similar to that reported by Gaubert et al (4) for the preparation of 5-pentenol from tetrahydrofurfuryl chloride. The yield of 6-hexenol was 65% with a b.pt. of 38-40°C at 2mm pressure.

6-Bromohexene

Fifty mls of a 4:1 w/w mixture of 6-hexenol and pyridine were added dropwise to 60 g. phosphorous tribromide (4). During this addition the reaction was maintained at approximately 0°C using an ice bath. The product was collected by distillation until white fumes appeared in the reaction vessel. The mixture was stirred mechanically during all of the above steps. The distillate was washed with both a 10% sodium hydroxide solution, and water then dried. The 6-bromohexene which boiled at 30-32°C at 3mm pressure was obtained in 40% yield.

6-Iodohexene

One hundred mls. of acetone containing 0.1 mole of 6-bromohexene and 25 g. of NaI was stirred for four hours. The reaction mixture was washed with water and extracted with several portions of ether. The combined ether layer was shaken with water, separated and dried over anhydrous potassium carbonate. The ether was removed by distillation to yield 65% of iodohexene which boiled at 55°C at 2mm of pressure.

Lithium dimethyl cuprate-¹³C

Methyl lithium was prepared from 0.08 moles of a mixture of unlabeled and labeled methyl iodide (the composition depending on the degree of labeling desired). The methyl lithium was filtered under dry nitrogen into a solution of 5 g. of cuprous iodide in dry ether. The solution was maintained at 0°C during this process. After addition of all of the dimethyl lithium the resulting solution of lithium dimethyl cuprate was gray in color.

Heptene-7-¹³C

Twenty-five mmoles of iodohexene in dry ether were added dropwise to the lithium dimethyl cuprate which had been allowed to warm to ambient conditions.

After addition was completed the mixture was stirred overnight. The resulting black solution was hydrolyzed with water and filtered. The filtrate was extracted with ether. The combined ether layer was washed with water and dried over anhydrous calcium chloride. The ether was removed by evaporation until a volume of 3 ml. was obtained. By GC analysis on a 6 ft. SE-30 column the peaks observed were ether and heptene.

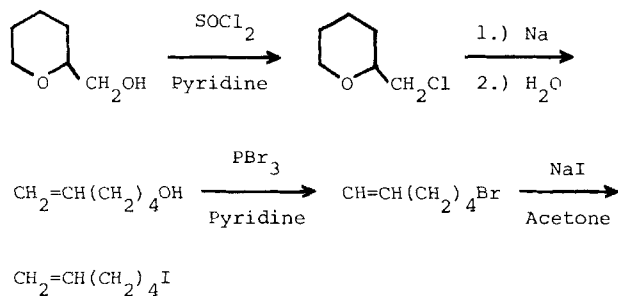
n-Heptyltrichlorosilane-7-¹³C

Four mls. of trichlorosilane, all of the above heptene, and 50 μ ls. of a 20% H_2PtCl_6 in isopropanol solution were placed in a stainless steel reaction vessel which was immersed in a dry ice acetone bath. After sealing, the reaction vessel was allowed to warm to ambient temperature. The vessel was then heated to 70°C and maintained at this temperature for eight hours. The average yield of labeled heptyltrichlorosilane monomer was 24% with a boiling point of 55°C at 2mm pressure.

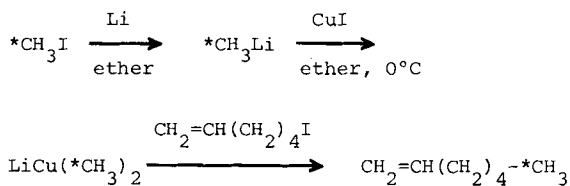
RESULTS AND DISCUSSION

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

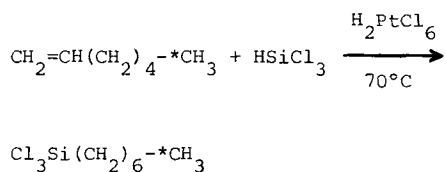
Step 1



Step 2



Step 3



The overall n-heptyltrichlorosilane-7-¹³C was produced in a 24% yield from methyl iodide, with essentially quantitative incorporation of the carbon 13 label.

| *CH ₃ I (mole) | CH ₃ I (mole) | CH ₂ =C(CH ₂) ₄ I (mole) | % Yield** | Enrichment | |
|---------------------------|--------------------------|--|-----------|------------|----|
| | | | | a | b |
| 0.007 | 0.08 | 0.025 | 25 | 9 | 9 |
| 0.004 | 0.08 | 0.025 | 21 | 4 | 4 |
| ----- | 0.08 | 0.025 | 25 | -- | -- |

*Labeled material

**Based on methyl iodide

^a Calculated from molar ratios

^b Determined from ¹³C NMR data

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