

SYNTHESIS OF ^{13}C LABELED n-ALKYLCHLOROSILANES

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SUMMARY

This report describes the synthesis of various carbon-13 enriched n-alkylchlorosilanes with label incorporation at selective positions along the alkyl chains. Compounds which were prepared were:

n-nonyltrichlorosilane-1- ^{13}C
n-dodecyltrichlorosilane-4- ^{13}C
n-dodecyltrimethylchlorosilane-4- ^{13}C
n-dodecyltrichlorosilane-12- ^{13}C
n-tridecyltrichlorosilane-12- ^{13}C
n-tridecyltrimethylchlorosilane-12- ^{13}C

Key Words: ^{13}C Labeled alkylchlorosilanes, ^{13}C -labeled alkyl-trimethylchlorosilane, reagents for labeling chromatographic surfaces, surface modification reagents.

INTRODUCTION

Not only has carbon magnetic resonance spectrometry been used to examine molecular dynamics, but the technique also has become popular to investigate surface adsorbed and bonded molecules. In the latter case such rigidly attached molecules produce broad resonance lines arising from hindered molecular mobility. For molecules with several methylene units, this results in resonance overlap in spectra acquired by conventional FT-NMR. Likewise in many cases, because such samples have

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relatively low amounts of attached carbon, spectral acquisition times may be prohibitively long. This is especially true of surface modified chromatographic materials. One approach to overcome these problems in resolution and sensitivity has been selective labeling of individual carbons along the chain (1,2,3).

The feasibility of using selective labeling in combination with various NMR experiments to examine chromatographic surfaces previously has been demonstrated. In this study the reactivity and attached layer was examined (1). Likewise the procedure for the synthesis of terminally labeled alkylchlorosilanes via methyl iodide (4) and barium carbonate routes (5) also have been reported. To continue the initial chromatographic and NMR studies (1) in more detail, various labeled chlorosilanes have been prepared with enrichment at the terminal and adjacent carbon positions as well as at the fourth and first methylenes.

EXPERIMENTAL

Carboxcyclic acids

Grignard compounds were prepared from either bromoalkenes (0.1 mole) or bromalkanes (0.1 mole) and magnesium turnings (0.12 mole) in ether. Subsequently these were reacted with carbon dioxide which was generated from a mixture of labeled and unlabeled barium carbonate according to the procedure reported by Dauben et. al, (6). The labeled acid, which was formed, was isolated by Gangoda and Gilpin (5) to yield (80-90%) of the labeled acid.

Alcohols

Labeled acids were reduced with lithium aluminum hydride according to the procedure reported by Heusler et. al, (7) to yield 0.028-0.41 mole (90-100%) of a given alcohol.

Bromoalkane

Labeled alcohols were treated with phosphorus tribromide also according to the procedure reported by Heusler et. al, (7) to yield 0.018-0.041 mole (75-80%) of bromoalkane.

Dodecene

Labeled bromonane was reacted with magnesium turnings to yield the corresponding Grignard reagent. The resulting solution was filtered and allyl bromide added. This mixture was then refluxed overnight and worked out according to the procedure reported by Wilkinson (8) to yield (90-95%) of dodecene-4- ^{13}C .

Tosylate

Unsaturated alcohols were reacted with tosylchloride in the presence of pyridine as reported previously (5) to yield 0.028-0.041 mole (90-95%) of the corresponding tosylate.

Iodoalkene

A given tosylate was treated with two equivalents of sodium iodide in acetone (9). The observed yield for the resulting iodoalkene was approximately (90-95%).

Dodecene

12-iodododecene-12- ^{13}C was refluxed with two equivalent of lithium aluminum hydride in ether overnight. Subsequently, excess hydride was destroyed with water and the reaction mixture then extracted with ether. The combined ether layers were dried over anhydrous calcium chloride, filtered and the ether removed by evaporation to yield 100% of dodecene-12- ^{13}C .

Tridecene-12- ^{13}C

Dodecenylytosylate-a- ^{13}C was reacted with two equivalents of lithium dimethyl cuprate according to the procedure reported by Johnson et. al, (10) to yield (70-80%) of tridecene-12- ^{13}C .

Chlorosilane

Labeled alkenes were reacted with trichlorosilane or with

dimethylchlorosilane as described in previous work (4). The observed yield of alkylchlorosilanes was about (80-85%).

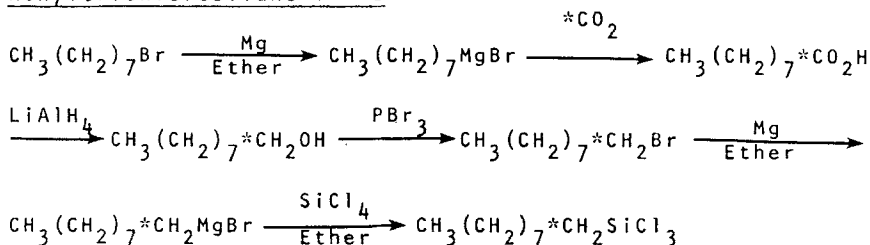
Nonyltrichlorosilane- ^{13}C

Excess silicon tetrachloride was reacted with labeled nonylmagnesium bromide according to the procedure reported by Whitmore, et. al, (12) to yield nonyltrichlorosilane- ^{13}C (75-80%).

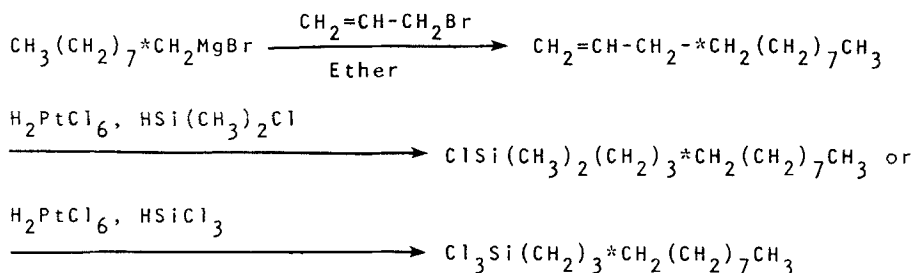
RESULTS AND DISCUSSION

The synthesis schemes that were employed are summarized in the following reaction sequences.

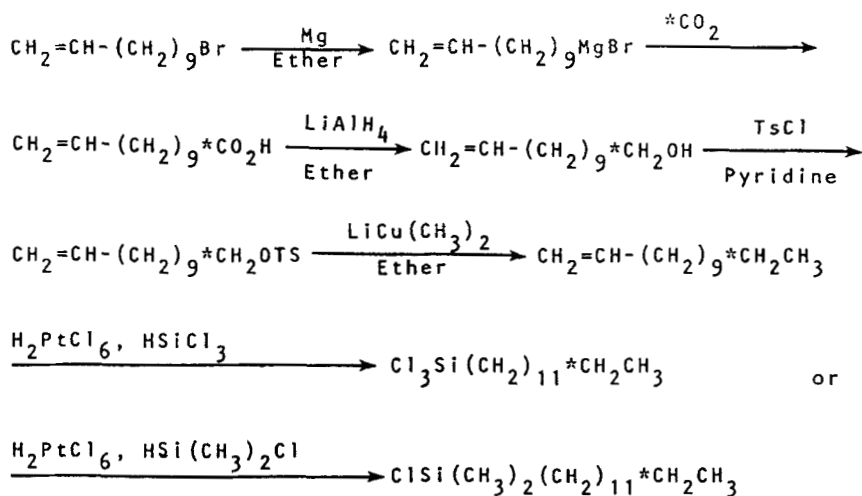
Nonyltrichlorosilane-1- ^{13}C



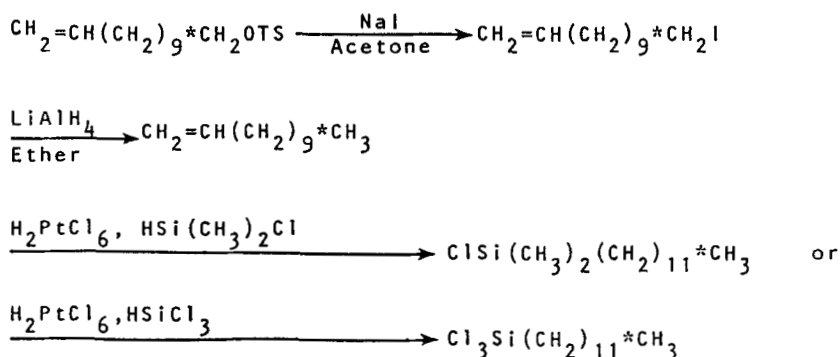
Dodecyltrichlorosilane-4- ^{13}C and Dodecyldimethylchlorosilane-4- ^{13}C



Tridecyltrichlorosilane-12- ^{13}C and
Tridecyl dimethylechlorosilane-12- ^{13}C



Dodecyltrichlorosilane-12- ^{13}C and
Dodecyl dimethylchlorosilane-12- ^{13}C



All intermediate reaction products were characterized by IR spectroscopy. Final chlorosilanes were examined by IR and carbon-13 NMR spectroscopy. The percentage incorporation of label was calculated by the method reported by Wright (11). In all cases quantitative incorporation was observed. The chemical shifts for the labeled carbon is given in the following table.

Silane	Chemical Shift
$\text{Cl}_3\text{Si}^*\text{CH}_2(\text{CH}_2)_7\text{CH}_3$	24.45
$\text{Cl}_3\text{Si}(\text{CH}_2)_3^*\text{CH}_2(\text{CH}_2)_7\text{CH}_3$	29.08
$\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_3^*\text{CH}_2(\text{CH}_2)_7\text{CH}_3$	29.29
$\text{Cl}_3\text{Si}(\text{CH}_2)_{11}^*\text{CH}_3$	14.13
$\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{11}^*\text{CH}_3$	14.14
$\text{Cl}_3\text{Si}(\text{CH}_2)_{11}^*\text{CH}_2\text{CH}_3$	22.72
$\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{11}^*\text{CH}_2\text{CH}_3$	22.72

The yields are summarized in the following table.

Compound	% Yield With Respect to Ba^*CO_3
$\text{Cl}_3\text{Si}^*\text{CH}_2(\text{CH}_2)_7\text{CH}_3$	42
$\text{Cl}_3\text{Si}(\text{CH}_2)_3^*\text{CH}_2(\text{CH}_2)_7\text{CH}_3$	52
$\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_3^*\text{CH}_2(\text{CH}_2)_7\text{CH}_3$	58
$\text{Cl}_3\text{Si}(\text{CH}_2)_{11}^*\text{CH}_3$	63
$\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{11}^*\text{CH}_3$	63
$\text{Cl}_3\text{Si}(\text{CH}_2)_{11}^*\text{CH}_2\text{CH}_3$	56
$\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_{11}^*\text{CH}_2\text{CH}_3$	58

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