Journal of Labelled Compounds and Radiopharmaceuticals—Vol. XXXIV, No. 5

Preparation of ^{14}C-labelled Dimethylsilane-1,1-diol

J.A. Cella and J.C. Carpenter

General Electric Company
Corporate Research and Development
PO Box 8, K1 4A50
Schenectady, NY 12301

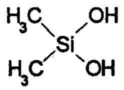
Summary

The preparation of ^{14}C-labelled dimethylsilane-1,1-diol in two steps from ^{14}C-labelled diphenyldimethylsilane is described. Aluminum chloride catalyzed protodesilylation of diphenyldimethylsilane with HCl in dichloromethane or dimethyldichlorosilane at 0-5°C affords labelled dimethyldichlorosilane which is hydrolyzed in the presence of triethylamine to afford the title compound in 45-60% yield.

Keywords: ^{14}C, dimethylsilane1,1-diol, protodesilylation

Introduction

Dimethylsilane-1,1-diol, **1**, the simplest monomeric unit of organosilicone polymers, is important as the principal water soluble environmental breakdown product of these materials(1). A radiolabelled derivative of **1** can be used to determine its environmental properties (adsorption-desorption equilibria, Henry's Law constants etc.) or to ascertain whether it is biodegraded *via* a pathway involving carbon-silicon bond cleavage.



1

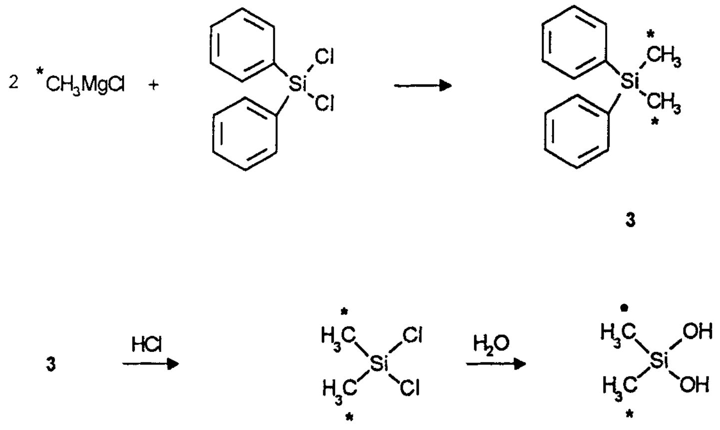
CCC 0362–4803/94/050427–04
©1994 by John Wiley & Sons, Ltd.

Received 8 October, 1993
Revised 15 December, 1993

Diol **1** is a rather labile compound, prone to self-condensation, even in the solid state if traces of acidic or basic impurities are present. The diol is generally prepared by hydrolysis of a suitable precursor, usually dimethyldichlorosilane, **2**, or an intermediate derived from it, under conditions which insure neutrality during preparation and workup (2). As dimethyldichlorosilane is itself a moisture sensitive, volatile compound, not readily prepared in pure form on a laboratory scale, a storage stable radiolabelled precursor was sought which could be transformed into **1** in a straightforward manner as needed.

^{14}C-labelled **2** has been prepared by $AlCl_3$ catalyzed protodesilylation of diphenyldichlorosilane, **3**, with HCl (3). Labelled **3** is available from the reaction of diphenyldichlorosilane and ^{14}C-methyl Grignard. The sequence depicted in Scheme 1 suited our needs well, since **3** is a storage stable intermediate.

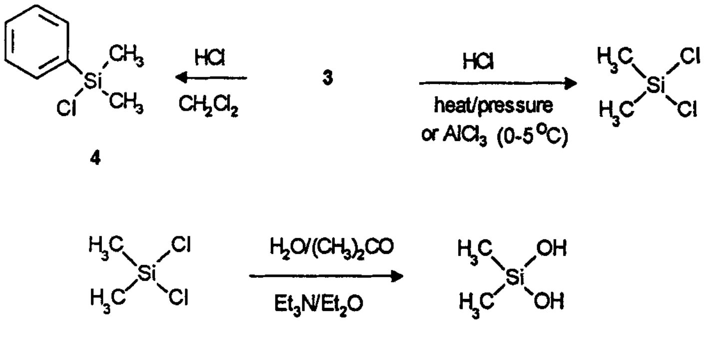
Scheme 1



3

2

For our purposes, the conversion of **3** to **2** was best carried out in dichloromethane or better, in cold dimethyldichlorosilane, which serves as both solvent and isotope diluent and obviates the need for solvent removal. In practice, the reaction of **3** with dry HCl in dichloromethane or dimethyldichlorosilane under ambient conditions in the absence of added catalyst affords phenyldimethylchlorosilane, **4**, the product of single protodesilylation of **3**. Further conversion of **4** to **2** requires warming the reaction mixture to 40 °C under autogenous pressure, an undesirable process when dealing with the radiolabelled species. In the presence of catalytic (1-2 mol%) $AlCl_3$, however, conversion of **3** to **2** with HCl is quantitative within 5 minutes at 0-5°C and ambient pressure. Excess HCl can be swept from the vessel with a stream of dry nitrogen affording **2** containing a trace of $AlCl_3$. The $AlCl_3$ is not detrimental to the subsequent hydrolysis step, which consists simply of addition of the protodesilylation reaction mixture to a chilled mixture of water (2.15 eq), triethylamine, (2.01-2.2 eq) and enough acetone to make the mixture homogeneous in diethylether(4). Diol, **1**, is obtained as a colorless solid in 50-70% yield (from **3**) after filtration of the reaction mixture, concentration of the filtrate and trituration of the residue with cold pentane. The pentane filtrate contains higher silanol terminated oligomers which may be useful in their own right as labelled silicone derivatives.



In summary, ^{14}C-labelled diphenyldimethylsilane is an ideal, storage stable precursor to dimethylsilane-1,1-diol *via* dimethyldichlorosilane. ^{14}C-labelled dimethyldichlorosilane can itself be a useful intermediate for the preparation of a variety of labelled organosilicon polymers and intermediates.

Experimental

Reagents- Dimethyldiphenylsilane and dimethyldichlorosilane were obtained from Huls-Petrarch and were distilled just prior to use. ^{14}C-dimethyldiphenylsilane (μ = 52.9 mCi/mmol, 98.3% isotopic purity) was obtained from Wizard Laboratories (Davis, CA). Triethylamine was obtained from Aldrich and used without further purification or drying.

Equipment High pressure liquid chromatography was carried out on a Perkin-Elmer series 410 HPLC pump interfaced to a Perkin-Elmer LC 30-RI refractive index detector or an LC-95 UV-Vis detector. A Whatman Partisil 10 ODS-3 column was employed with isocratic 80% acetonitrile-20% water as the eluant at a flow rate of 1.5 ml./min. NMR spectra were determined on a GE NMR Instruments QE-300 instrument operating at a frequency of 75.4 MHz for ^{13}C spectra and 300MHz for proton spectra. Infrared Spectra were determined using a Mattson Instruments Galaxy Series FT-IR Model 6020 instrument. Scintillation counting was carried out on a LKB Model 1214 Rackbeta Scintillation Counter.

Preparation of ^{14}C-dimethyldichlorosilane, 2, from ^{14}C-dimethyldiphenylsilane, 3: Depending on the specific activity desired, ^{14}C-diphenyldimethylsilane was dissolved in dimethyldichlorosilane in a two-neck flask fitted with a gas inlet tube and a condenser. The flask was immersed in an ice-water bath and anhydrous aluminum chloride (1 mole % relative to diphenyldimethylsilane) was added. Dry HCl gas was bubbled through the chilled mixture at a moderate rate for about two minutes or until the solution becomes saturated. The resulting solution was stirred cold for an additional hour (NMR analysis indicates the reaction is complete within 5 minutes). Dry nitrogen was then passed through the reaction mixture for 2 minutes to purge excess HCl, care being taken to avoid sweeping out the dimethyldichlorosilane product by use of an efficient condenser. The contents of this flask were used directly in the next step.

Preparation of ^{14}C-dimethylsilanediol, 1. Dichlorodimethylsilane, 28g (217 mmol) in 25 ml. of ethyl ether was added dropwise with stirring to a 0 °C solution consisting of 48.2 g. (477 mmole, 2.2 equiv.)of triethylamine , 8.4 g. (466.6 mmole, 2.15 equiv.)of water , 250 ml. ethyl ether and enough acetone (≈40 ml.) to provide homogeneity. Addition of chlorosilane was complete in 1.0 hr. Following addition the solution was allowed to stir for an additional 30 minutes at 0 °C. The triethylamine hydrochloride was removed by vacuum filtration and the filtrate was concentrated to one-tenth its volume by evaporation in a stream of dry nitrogen. At this point pentane, ≈200 ml was added to the flask and evaporation was continued. The solid was collected by filtration and washed with cold pentane to remove any residual triethylamine. Crude dimethylsilanediol, 9.6 g grams (48%), was obtained, m.p. = 93-96 °C. The identity of labelled **1** was confirmed by comparison of its spectral (^{1}H NMR, Mass spectrum (m/e 77 (M$^+$-15)) and chromatographic identity with an authentic sample. The specific activity of the diol obtained in this fashion was determined by scintillation counting to be 27.6 µCi/mmol)

References

1. (a) Lehmann, R., Varaprath, F. and Frye, C.L., Environ. Toxicol. Chem., xxxx: (1994) (in press). (b) Cella J., et al, Abstracts National ACS Meeting, Denver, CO (1992). Buch, R.R.and Ingebrigston, D.N., Env. Sci. Tech., 13: 676 (1979).
2. (a) Hyde, J.F., J. Am. Chem. Soc., 75: 2166 (1953). (b) Kantor, S.W., J. Am. Chem. Soc.,75: 2712 (1953). (c) Daudt, W.H. and Hyde, J.F., J. Am. Chem. Soc., 74: 3861 (1952).3. Frisch, K.C., Goodwin, P.A. and Scott, R.E., J. Am. Chem. Soc., 74: 4584 (1952). (e) Sauer, R.O. J. Am. Chem. Soc., 66: 1707 (1944) (f) Whitmore, F.C., Sommer, L.H.and DiGiorgio, P.A., J. Am. Chem. Soc., 68, 344 (1946). (g) George, P.D., Sommer, L.H. and Whitmore, F.C., J. Am. Chem. Soc., 75: 1585 (1953).(h) Harris, G.I., J. Chem. Soc.: 5978 (1963). (i) Takiguchi, T., J. Am. Chem. Soc., 81: 2359 (1959).
3. Vidal, A., Joachim, F. and Papirer, E., J. Labelled Comp. and Radiopharm., 28: 455 (1990).
4. Cella, J.A., and Carpenter,J.C., J. Organomet. Chem., xxxx: (1994) (in press).