Journal of Labelled Compounds and Radiopharmaceuticals—Vol. XXVIII, No. 4

SYNTHESIS OF TETRAMETHYLETHYLENEDIOXYDI-[^{14}C]-METHYLSILANE

Alain VIDAL*, Francis JOACHIM** and Eugène PAPIRER

Centre de Recherches sur la Physico-Chimie des
Surfaces Solides - CNRS
24, avenue du Président Kennedy
68200 MULHOUSE (FRANCE)

SUMMARY

The synthesis of tetramethylethylenedioxydi-[^{14}C]-methylsilane, a molecule used as a plasticizer in polysiloxane/silica blends, is described. This compound was synthesized in a 48 % overall radiochemical yield from [^{14}C]-methyl iodide and with a specific radioactivity of 33 µCi/mmole. It was used to study the competitivity of adsorption of plasticizers and models of polydimethylsiloxanes towards silicas.

Key words : Antistructurizing agent, Tetramethylethylenedioxydimethylsilane, di-[^{14}C]-methyldichlorosilane, di-[^{14}C]-methyldiphenylsilane.

INTRODUCTION

Crosslinked high molecular weight linear disubstituted polysiloxanes such as polydimethylsiloxane (PDMS) only exhibit tensile strength in the range of about 0.34 MPa (1), a value which is of course too low to satisfy the property requirements of most applications. Such shortcomings can however be compensated by compounding the corresponding silicone elastomers with high surface particulate solids such as amorphous silicas. Such a blending is associated not only with an improvement of the physical properties of the resulting compounds but also with a stiffening of the corresponding materials which is known as "crepe hardening". Such an effect which results from the occurence of very strong interactions at the silica/polymer interface can

---

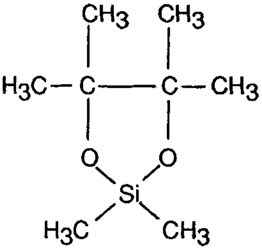
* Author to whom correspondence should be addressed
** Present address : Rhône-Poulenc Recherches, Centre de Recherches des Carrières, 69192 SAINT FONS CEDEX (FRANCE)

0362–4803/90/040455–06$05.00

Revised October 25, 1989

be deleterious for the processing of the filled elastomers. Numerous investigations have been devoted to the interpretation of such a phenomenon (2-6) which can be overcome either by use of plasticizers also called antistructurizing agents (usually low molecular weight silanes and siloxanes) or by pretreatment of the reinforcing filler (2).

In order to assess the role played by plasticizers during the processing of silica/polysiloxane blends we have studied the competitivity towards silicas of a particular plasticizer [tetramethylethylenedioxydimethylsilane (1) = AS] and of models of PDMS. For analytical purposes (ease of titration by β spectrometry) we had to synthesize a [^{14}C]-labelled AS.

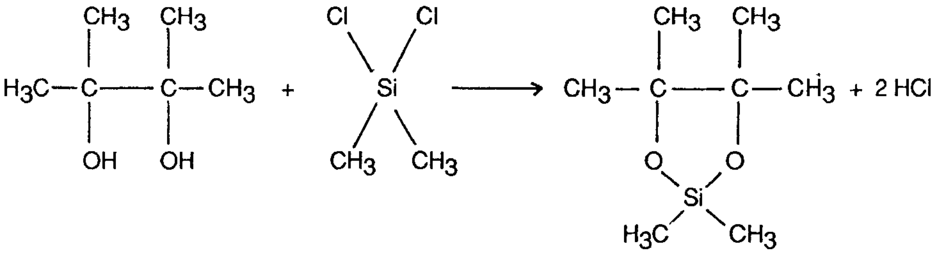


1

DISCUSSION

Our approach to the synthesis of AS was to react dimethyldichlorosilane (2) with 2,3-dimethyl-2,3-butanediol (3) according to reaction scheme 1.

SCHEME 1



The best approach to ^{14}C labelling of AS was to use di-[^{14}C]-methyldichlorosilane which was synthesized from [^{14}C]-methyl iodide as outlined in reaction scheme 2.

SCHEME 2

$$^{14}CH_3I + Mg \xrightarrow{Et_2O} {}^{14}CH_3MgI$$

4

$$2\ ^{14}CH_3MgI + (C_6H_5)_2SiCl_2 \xrightarrow{\qquad} \underset{\underline{5}}{(C_6H_5)_2Si(^{14}CH_3)_2} + 2\ MgICl$$

$$(C_6H_5)_2Si(^{14}CH_3)_2 + 2\ HCl \xrightarrow[C_6H_6]{AlCl_3} \underset{\underline{2}}{(^{14}CH_3)_2SiCl_2} + 2\ C_6H_6$$

The first step corresponding to the preparation, in presence of diethylether, of [^{14}C]-methylmagnesium iodide (4) is followed by a condensation of 4 onto diphenyldichlorosilane (5). Under mild conditions the latter is reacted in benzene solution with hydrogen chloride (aluminum trichloride being used as a catalyst) which gives di-[^{14}C]-methyldichlorosilane (2). This reaction step has to be carefully controlled since $AlCl_3$ is able to catalyze redistribution reactions between chlorosilanes thus inducing the formation of mono and trichloro derivatives (7). For this purpose 5 is added dropwise under HCl flushing to a reaction medium which has to be continuously HCl saturated and whose temperature must never exceed 15 °C.

The last step of the [^{14}C]-AS synthesis corresponds to the condensation in benzene solution of 2 onto pinacol (3) in presence of an organic base such as triethylamine (8). The role of the latter is, by reaction with evolved HCl, to avoid the presence of any free acid which would induce secondary reactions and thus lower reaction yields.

After each step of the synthesis, the resulting compounds were purified by fractional distillation. In some instances, separation of the reactants from the reaction medium was not deemed necessary because the same solvent was used in the following stage. This was particularly the case for the reaction of [^{14}C]-methyl magnesium iodide with diphenyldichlorosilane which as the synthesis of the Grignard reagent was performed in ether, and for the last step of the [^{14}C]-AS preparation which as the obtention of the di-[^{14}C]-methyldichlorosilane was performed in benzene. All compounds were characterized by IR and NMR spectroscopy. Their activities were assessed by β spectrometry.

Quantity and activity of the reactants used at the start of the reaction were selected so as to get, after completion of the synthesis, 25 to 30 ml of [^{14}C]-AS with an activity in the 4 to 5 mCi range. The experiment provided effectively 25 ml of [^{14}C]-AS with an activity of 4.1 mCi and a yield (with regard to [^{14}C]-methyl iodide) equal to 48 % (74 % compared to dimethyldichlorosilane). Yields and activities corresponding to intermediate steps of the reaction were the following :

- di-[^{14}C]-methyldiphenylsilane : 82 % compared to diphenyldichlorosilane, 74 % compared to [^{14}C]-methyl iodide; activity : 6.74 mCi;
- di-[^{14}C]-methyldichlorosilane : 84 % compared to di-[^{14}C]-dimethyldiphenyl silane; activity : 5.56 mCi.

Purity of synthesized [^{14}C]-AS was assessed by ^{1}H-NMR spectrometry from the ratios of the surface areas of the peaks corresponding to H bound to C (H_C) and Si (H_{Si}) atoms, respectively. The experimental value was found to be $H_C/H_{Si} = 2.1$, to be compared with a theoretical value of $H_C/H_{Si} = 2$.

EXPERIMENTAL

Reactants

[^{14}C]-methyl iodide was supplied by the CEA (France), with a specific activity in the 45 to 50 mCi/mmole range. All other reactants except hydrogen chloride (Air Liquide, purity > 99.99 %) were supplied by Merck (synthesis grade).

Synthesis of di-[^{14}C]-methyldiphenylsilane

[^{14}C]-methylmagnesium iodide

[^{14}C]-methyl iodide (5 ml, 1.69 mCi, 21 mCi/mole) in dry ether (12 ml) was added to dry magnesium turnings (15 g) in dry ether (30 ml) under nitrogen. The reaction flask was hand warmed to start the reaction and then a further quantity of [^{14}C]-methyl iodide (20 ml, 6.75 mCi, 21 mCi/mole) in ether (48 ml) was added dropwise under stirring at such a rate that the mixture refluxed gently. When the reaction became too vigorous, the flask was cooled in ice water.

After complete addition of the [^{14}C]-methyl iodide solution, a further quantity of the carrier methyl iodide (12 ml) in ether (30 ml) was slowly added. Then temperature of the reaction medium was 50 °C and 3 hours had elapsed since the beginning of the reaction. Finally, the reaction mixture was refluxed until all, or most, of the magnesium had reacted (about 5 hours). The ethereal solution of [^{14}C]-methyl magnesium iodide, forming a mobile liquid of a slate-grey colour, was used directly for the next stage of the synthesis.

di- [^{14}C]-methyldiphenylsilane

The ethereal solution of the [^{14}C]-labelled Grignard reagent was allowed to cool. Then, a solution of diphenyldichlorosilane (68.3 g, 56 ml, 0.27 mole) in anhydrous ether (30 ml) was slowly added under vigorous stirring. The rate of addition of the reactant was such as to prevent any increase of the temperature of the reaction medium above 65 °C, cooling the flask in cold water if necessary. When the addition of diphenyldichlorosilane was completed (~ 2.5 hours) the reaction medium was refluxed for 30 minutes. After cooling to room temperature, the ethereal solution was poured slowly with stirring onto crushed ice. The upper light-yellow ethereal layer was then separated and the aqueous phase was extracted with ether (30 ml). The combined ethereal extracts were dried over anhydrous calcium chloride, then ether was evaporated and the residue was distilled under vacuum (rotating strip column : 1 m long). The heart-cut (47 ml) was collected at 106 °C under reduced pressure (1.09 mm of mercury) to yield the product in a 82 % yield from diphenyldichlorosilane (74 % calculated from [^{14}C]-methyl iodide).

This compound was characterized by β spectrometry (activity) and NMR spectroscopy (structure control). The corresponding ^{1}H-NMR spectrum (80 MHz, CCl_4) exhibits 3 peaks whose chemical shifts from tetramethylsilane (TMS) are 0.52 ($C\underline{H}_3$-), 7.27 (o,p-$C_6\underline{H}_5$) and 7.45 ppm (m-$C_6\underline{H}_5$), respectively. Using the integrated areas from aromatic (A) and aliphatic protons (B), it was possible to confirm the obtention of the desired compound. Experimental A/B was indeed equal to 1.77 while the theoretical A/B calculated from the formula of dimethyldiphenylsilane should be 1.67. The radiochemical activity of the resulting product was measured by β spectrometry (6.74 mCi), it gave an overall radiochemical yield of 79.9 % from $[^{14}C]$-methyl iodide.

Synthesis of di-$[^{14}C]$-methyldichlorosilane

Anhydrous benzene (46 ml) was saturated with hydrogen chloride in presence of $AlCl_3$ (~ 0.8 g, ground under inert atmosphere) and while HCl bubbling and after setting the temperature of the reaction medium at 15 °C, di-$[^{14}C]$-methyldiphenylsilane (46 ml, 6.6 mCi) was added dropwise with stirring from a dropping funnel (~ 2 hours). Care was taken never to exceed 15 °C and to continuously have an HCl saturated solution. When the addition of di-$[^{14}C]$-methyldiphenylsilane was completed, HCl in excess was driven away by nitrogen flushing. Any attempts to separate the di-$[^{14}C]$-methyldiphenylsilane from the reaction medium (~ 100 ml, yellow in colour) by distillation (rotating strip column) failed. As shown by NMR spectroscopy, benzene was indeed present in each of the separated fractions. In the aromatic region of the spectra only one peak was detected at $\delta = 7.17$ ppm from TMS. Such a result suggested the absence of any substituted aromatic nuclei and as a consequence the obtention of the desired di-$[^{14}C]$-methyldichlorosilane. Another peak centered at 0.55 ppm from TMS was due to the protons of methyl groups. By comparison of the integrated areas of the peaks corresponding to the aromatic and aliphatic protons, it was possible to estimate the amount of dimethyldichlorosilane obtained, i.e. 22.3 ml (23.7 g). Reaction yield calculated from di-$[^{14}C]$-methyldiphenylsilane was 84 % and the radiochemical activity of the resulting product was shown to be equal to 5.56 mCi which gave an overall radiochemical yield of 84 % from di-$[^{14}C]$-methyldiphenylsilane.

Synthesis of tetramethylethylenedioxydi-$[^{14}C]$-methylsilane ($[^{14}C]$-AS)

The previously prepared solution of di-$[^{14}C]$-methyldichlorosilane (22 ml) in benzene (77 ml) was slowly added (dropping funnel) under stirring to a solution of pinacol (21.5 g, 0.18 mole) in triethylamine (93.5 ml, 0.67 mole). At once, the reaction medium became cloudy, while its temperature increased to about 60 °C. After addition was complete (~ 45 minutes) an important orange-pink precipitate was obtained and stirring was continued, first for 5.5 hours at room temperature, then under reflux (87 °C) for 4 hours. After cooling to room temperature and filtration (sintered glass filter crucible), the triethylamine hydrochloride salt was repeatedly washed with benzene (150 ml). The combined corresponding filtrates were distilled (rotating strip column). Two fractions could be separated. Their boiling points were 77.5 and 144 °C (746 mm Hg) and these were identified as benzene and $[^{14}C]$-AS, respectively. The latter fraction contained needle like crystals which were separated by decantation. They were shown, by IR and NMR spectroscopy, to be due to unreacted pinacol. The obtention of [^{14}C]-AS (about 25 ml) was confirmed by IR and NMR spectrometry. Its NMR spectrum showed indeed the presence of two peaks whose chemical shifts from TMS are 0.52 and 1.57 ppm respectively. They are attributed to protons of methyl groups bound to silicon (H_{Si}) and carbon atoms (H_C), respectively. Their ratio (H_C/H_{Si} = 2.1, theoretical value = 2) confirmed the obtention of AS. Reaction yield calculated from dimethyldichlorosilane was 74 %. The radiochemical activity of the obtained [^{14}C]-AS was shown to be equal to 4.09 mCi which corresponds to an overall radiochemical yield of 74 % from di-[^{14}C]-methyldichlorosilane and 48 % from [^{14}C]-methyl iodide.

REFERENCES

1. Polmanteer K.E. - Rubber Chem. Technol., 54 : 1051 (1981).
2. Warrick E.L., Pierce O.R., Polmanteer K.E. and Saam J.C. - Rubber Chem Technol., 52 (3) : 437 (1979).
3. Berrod G., Vidal A., Papirer E. and Donnet J.B. - J. Appl. Polymer Sci., 23 (9) : 2579 (1979); - Ibid., 26 : 833 (1981); - Ibid., 26 : 1015 (1981).
4. Chahal R.S. and Saint Pierre L.E. - Macromolecules, 1 (2) : 152 (1968).
5. Ashmed B.V. and Owen M.J. - J. Polymer Sci., A2 (9) : 331 (1971).
6. Perkel P. and Ullman R. - J. Polymer Sci., 54 : 127 (1961).
7. Belzung M. - Ph. D. Thesis, Strasbourg 1982.
8. I.C.I. - French Patent n° 1.169.094 (1958).