Silicon-assisted etherification reactions: application to the synthesis of high-molecular-weight polyethers

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The formation of ether bonds by reaction of benzylic bromides with phenyl silyl ethers has been investigated as an alternative to the classical Williamson ether synthesis. The reaction has been applied to the synthesis of high-molecular-weight polyethers that are not readily obtained by other methods. An AB-type monomer, such as 3-bromomethyl-trimethylsilyloxybenzene, reacts in the presence of a stoichiometric amount of carbonate to afford the corresponding polyether with molecular weight as high as 300 000 depending on the reaction conditions. While the polyetherification reaction of 3-bromomethyi phenol under classical conditions leads to polymers rich in C-alkylated and branched units, conditions may be found to reduce or prevent C-alkylation and branching with 3-bromomethyl-trimethylsilyloxybenzene. The reaction is believed to proceed via activation of the O–Si bond through carbonate addition to afford a species containing a pentacoordinate silicon. The role of carbonate and the stoichiometry and mechanism of the reaction have been investigated with the help of a model etherification reaction.

(Keywords: etherification; silicon; high-molecular-weight polyethers)

INTRODUCTION

Our recent studies on the convergent synthesis of regular dendritic polyethers[1] have made extensive use of the classical Williamson ether synthesis. Overall the synthesis involves a series of repetitive etherification reactions with intermediate purification and activation steps. An alternative approach to somewhat analogous hyperbranched polyethers involves the direct polycondensation of an AB_2 monomer such as 5-bromomethyl-1,3-dihydroxybenzene under typical phase-transfer catalysis conditions[2,3]. This approach provides structures that are much less regular than those made by the stepwise, convergent-growth process but it allows the preparation of large amounts of material in a single step[2–6]. However, a recurring problem is that the standard Williamson polyetherification reaction is limited to the production of relatively low-molecular-weight materials as precipitation sometimes occurs as early as at the oligomeric stage. Because high-molecular-weight materials are frequently desirable, this report concerns an alternative route to the classical polyether synthesis that may afford polymers with higher degrees of polymerization.

The preparation of polyethers under phase-transfer catalysed conditions has attracted some attention[7] since fairly mild conditions can be employed. For example, the polycondensation of bisphenol A with dibromoxylene in a two-phase system[7] in the presence of 18-crown-6 affords a polyether, said to be linear, with a molecular weight of 4500. This molecular weight is not atypical for the polycondensation of diphenols with dihalides under phase-transfer conditions as products with molecular weights from 5000–6000 have been reported[7,8] in several instances. Higher-molecular-weight polymers can conveniently be obtained by using dichloromethane as the solvent[9,10]. In this case, dichloromethane itself reacts to link together the ether oligomers that are initially formed, affording a heterogeneous structure containing not only ether bonds but also some acetal bonds interspersed throughout the polymer. These mixed poly(formalethers) have been reported with molecular weights as high as 700 000.

We have recently found that ether formation proceeds readily upon reaction of a trimethylsilyl-substituted phenol with an alkyl halide in the presence of base[11]. This reaction is investigated in this report and its application to the synthesis of high-molecular-weight polyethers is explored.

EXPERIMENTAL

General directions

Ultra-violet (u.v.) spectra were recorded in acetonitrile on a Nicolet UV/Visible 9420/9430 spectrophotometer. ^1H n.m.r. spectra were recorded on solutions in $CDCl_3$ or d_6-acetone on a Brücker WM300 spectrometer at 300.13 MHz using the solvent proton signal as reference.

^{29}Si n.m.r. spectra were recorded on a Brücker WM300 spectrometer operating at 59.6 MHz for ^{29}Si. A small amount (~ 100 mg) of chromium(III) acetylacetonate was added as a relaxation reagent to shorten the ^{29}Si spin-lattice relaxation times (T_1), and gated decoupling was used to eliminate the negative nuclear Overhauser effect. All ^{29}Si chemical shifts are reported relative to

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internal tetramethylsilane with positive values to lower field (deshielded) and negative values to higher field (shielded).

Gas chromatography was performed on an HP5890A gas chromatograph; data analysis was performed on an HP3392A integrator. Analytical thin-layer chromatography (t.l.c.) was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Gel permeation chromatography was carried out on a Nicolet LC/9560 liquid chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector. Data analysis was performed using Viscotek GPC-PRO software. Three PLgel columns (Mixed-C) connected in series were used with tetrahydrofuran (THF) as solvent. Columns were calibrated using narrow dispersity polystyrene standards.

Reagents

All carbonates, bicarbonates and potassium fluoride were dried over P_2O_5 under vacuum at 120°C. Tetrabutylammonium fluoride in THF (1.0 M) was purchased from Aldrich Chemical Co. and used without further purification. Tetrabutylammonium benzoate and bibenzoate were prepared according to a published procedure[12]. Benzyl bromide and dichloromethane were purified by simple distillation. Acetonitrile was heated to reflux over CaH_2, distilled and then stored over CaH_2. Acetone was heated to reflux over dried K_2CO_3, distilled and stored over dried K_2CO_3. Tetrahydrofuran was heated to reflux over metallic sodium and benzophenone, and distilled prior to use.

Preparation of 3-bromomethylphenol[13], 1

Triphenylphosphine (5.93 g, 22.6 mmol) was added slowly to a stirred solution of 3-hydroxymethylphenol (2.52 g, 20.3 mmol) and carbon tetrabromide (7.49 g, 22.6 mmol) in freshly distilled THF (35 ml) under nitrogen. After 100 min, the solvent was removed and the product purified by flash chromatography with 1:1 dichloromethane:ethyl ether as the eluent to give 2.26 g of white solid (59% yield). ^1H n.m.r., ($CDCl_3$): δ 4.44 (s, 2H, CH_2), 4.83 (br, 1H, OH), 6.76 (m, 1H, ArH), 6.79 (t, 1H, ArH), 6.96 (m, 1H, ArH), 7.22 (t, 1H, ArH). ^{13}C n.m.r., ($CDCl_3$): δ 33.4, 115.0, 115.5, 120.8, 129.8, 139.1, 156.0.

Preparation of 3-bromomethyl-trimethylsilyloxybenzene, 3

Bromotrimethylsilane (14 ml, 110 mmol) was added to a slurry of 3-hydroxymethylphenol (6.3 g, 51 mmol) in chloroform (15 ml). After 80 min, the reaction solution was evaporated to dryness. Hexamethyldisilazane (23 ml, 110 mmol) and chlorotrimethylsilane (1.0 ml, 7.9 mmol) were added to the reaction mixture. After heating to reflux for 2.5 h, the solvent was removed and the product was distilled in an oil bath at 125°C under 0.3 mmHg to give 7.1 g of clear oil (54% yield). ^1H n.m.r., ($CDCl_3$): δ 0.26 (s, 9H, Si–CH_3), 4.42 (s, 2H, CH_2), 6.7–7.2 (m, 4H, ArH). ^{13}C n.m.r., ($CDCl_3$): δ 2.5, 33.3, 120.0, 120.7, 122.3, 129.7, 139.2, 155.4.

Preparation of 2 by polycondensation of monomer 3

Caesium carbonate (3.8 g, 12 mmol) was added to a solution of **3** (2.0 g, 7.8 mmol) in freshly distilled THF (6 ml). The reaction mixture was heated to reflux for 14 h, filtered, washed with THF, and the filtrate concentrated. The polymer was purified by precipitation from dimethylformamide into diethyl ether to give 0.65 g of yellow solid (76% yield). The precipitation step leaves a low-molecular-weight polymer in solution. These low-molecular-weight fractions were found to have essentially the same compositions (C- *versus* O-alkylation) as the corresponding precipitated material reported in *Table 1*.

Preparation of trimethylsilylphenol, 5

Chlorotrimethylsilane (8.0 ml, 60 mmol) was added to a slurry of phenol (48 g, 51 mmol) in hexamethyldisilazane (110 ml). The reaction mixture was heated to reflux for 2 h under nitrogen, the solvent was then removed and the product distilled at 180°C to give 64 g of clear oil (75% yield). ^1H n.m.r., ($CDCl_3$): δ 0.24 (s, 9H, Si–CH_3), 6.8–6.9 (m, 3H, ArH), 7.16–7.22 (m, 2H, ArH).

Preparation of bis-(trimethylsilyl)resorcinol

Chlorotrimethylsilane (4.0 ml, 30 mmol) was added to a slurry of resorcinol (27 g, 250 mmol) in hexamethyldisilazane (110 ml). The reaction mixture was heated to reflux for 2 h under nitrogen, the solvent was then removed and the product distilled by heating to 250°C in an oil bath to afford 36 g of clear oil (57% yield). ^1H n.m.r., ($CDCl_3$): δ 0.30 (s, 18H, $SiCH_3$), 6.41 (t, 1H, ArH), 6.51 (m, 2H, ArH), 7.09 (t, 1H, ArH).

RESULTS AND DISCUSSION

Polymerization of an AB monomer by Williamson polyetherification

For comparison purposes, the preparation of a polyether from an AB type monomer, 3-bromomethylphenol **1**, under classical Williamson synthesis conditions was investigated. This new monomer was prepared from commercially available 3-hydroxymethylphenol by bromination with carbon tetrabromide and triphenylphosphine (*Scheme 1*). Using the phase-transfer conditions described in the literature[7,8] (*Table 1*), monomer **1** gave polymer **2** in 78% yield with a gel-permeation chromatography (g.p.c.) weight-average molecular weight of 11 000 (values given are polystyrene equivalent $\bar{M}_w$). Under analogous conditions in homogeneous medium with caesium carbonate in refluxing THF, **1** gave a polyether with a molecular weight of 8000 in 94% yield. Both of these results are consistent with the literature in

Table 1 Preparation of **2** by the polycondensation of monomer **1**

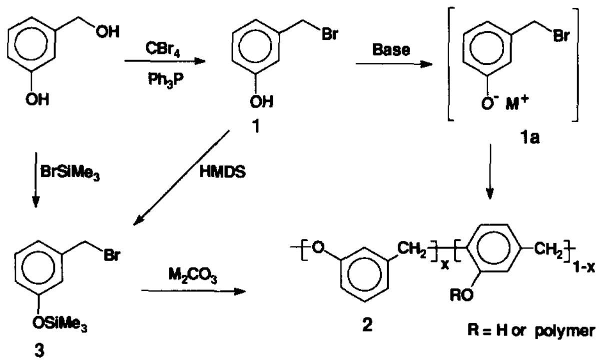
Entry	Reagent	Solvent	Temp. (°C)	Time (h)	Yield (%)	$\bar{M}_w$	$\bar{M}_n$	C-alkyl (%)
1	KOH/Bu_4NHSO_4	3-methyl-2-butanone	95	15	78	11 300	3800	39
2	Cs_2CO_3	THF	67	19	94	8 000	1800	20

which similar reactions usually lead to polyethers of relatively modest molecular weights[7,8].

N.m.r. analysis of the polyethers shows that a significant amount of C-alkylation occurs during polycondensation to afford a polymer having structure **2** (*Scheme 1*) where $0<x<1$ (*Table 2*). The occurrence of C-alkylation is readily confirmed by ^1H n.m.r. spectroscopy as a methylene peak is seen at 4.0 ppm in addition to the expected ether methylene peak at 5.0 ppm. This side-reaction is not unexpected in view of the mechanism of etherification that involves intermediate phenoxide ions. The C-alkylation side-reaction is troublesome because it effectively transforms the difunctional AB monomer units incorporated into the C-alkylated sites, into trifunctional ABB′ units that can give rise to branching.

Silicon-assisted polymerization

In view of these findings, the use of silicon-assisted chemistry[11] was investigated as it appeared capable of producing more regular and higher-molecular-weight polymers than the classical condensations involving phenols. Silyl ethers have been used to aid other types of polycondensations. In particular, Kricheldorf has used silylated phenols in the preparation of poly(ether sulfones) and poly(ether ketones)[16–18]. In his approach, silylated phenols were condensed with aromatic difluorides in the presence of CsF via nucleophilic aromatic substitution at temperatures exceeding 250°C to give products with molecular weights as high as 60 000. The main advantage of the use of silyl ethers in this process is that higher-molecular-weight products are obtained in higher yields, although the reaction conditions are very harsh.



Scheme 1

The AB-type monomer selected to test our polycondensation was 3-bromomethyl-trimethylsilyloxybenzene, **3**. It is prepared from 3-bromomethylphenol **1** by halide ion catalysed silylation with hexamethyldisilazane (HMDS) or, more directly, from the commercially available 3-hydroxymethylphenol (*Scheme 1*). In the latter procedure, bromotrimethylsilane is used to transform the benzylic alcohol into the corresponding bromide. HMDS is added before work-up to ensure that all of the phenolic groups are protected as their trimethylsilyl ether derivative and the final product **3** is isolated by vacuum distillation.

Many different reagents were tested to effect the polycondensation of **3** (*Table 2*). Initial experiments involved the use of fluoride ion because it is a common reagent for reactions involving silylated compounds. Though quantitative, the polycondensation of **3** using KF and 18-crown-6 in refluxing THF only afforded a polyether with a molecular weight of 7000, clearly not a significant improvement over the classical polycondensation, although the product is a true polyether (structure **2**, $x=1$).

The polycondensation of **3** was then attempted in the presence of carbonate ions under phase-transfer conditions (*Table 2*, entries 5, 6). The use of potassium carbonate and 18-crown-6 in acetone or THF afforded polyether **2** with molecular weights of 11 000 and 38 000, respectively, in modest yields varying from 60 to 65%. These results are encouraging because a significant increase in molecular weight is achieved over the conventional Williamson-type polycondensation (*Table 1*) and the product **2** that is isolated is totally free of C-alkylation ($x=1$ in *Scheme 1*). This finding is particularly important as it probably means that the polyether is free of the sort of branching that undoubtedly affects all C-alkylated polymers prepared from **3** or **1**.

The combination of caesium carbonate and DMF has been used by Kellog *et al.*[16,17] for a number of nucleophilic displacement reactions including etherification reactions; however, this combination proved disappointing in the polymerization of **3** as it only afforded low-molecular-weight polymers (*Table 2*). A different combination of caesium carbonate with THF, a solvent of lower polarity, proved to be extremely successful, affording polyether **2** ($x=0.91$) with a molecular weight of more than 300 000 in 76% yield. This polycondensation using caesium carbonate in THF is successful even at

Table 2 Preparation of **2** by the polycondensation of monomer **3**

Entry	Reagent	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)	C-alkyl (%)	G.p.c. $\bar{M}_w$	G.p.c. $\bar{M}_n$
3	KF	18-c-6	THF	67	15	99	0	7 300	5 200[a]
4	KF	18-c-6	THF	67	8	88	0	3 300	2 900[b]
5	K_2CO_3	18-c-6	Acetone	56	16	62	0	11 400	9 000
6	K_2CO_3	18-c-6	THF	67	19	63	0	38 000	20 000[c]
7	Cs_2CO_3	–	DMF	65	24	50	0	5 300	2 300[a]
8	Cs_2CO_3	–	THF	67	14	76	9	315 000	70 000[c]
9	Cs_2CO_3	–	THF	23	18	90	18	290 000	65 000
10	TMSOK	–	THF	67	2	95	33	225 000	87 000[b]

[a] Polyether precipitated from hexane
[b] Reagent is added slowly to the reaction mixture
[c] Polyether precipitated from diethyl ether

room temperature although the polymer that is obtained ($M_w = 290000$, 90% yield) contains a higher proportion of C-alkylated units ($x = 0.82$).

Because the carbonate ion is a weaker nucleophile than the fluoride ion, it is possible that the outcome of the polymerization is affected by the relative concentration of free phenoxide ion during the course of the polymerization. However, an experiment in which the required amount of fluoride was added slowly to a solution of monomer **3** over an 8 h period was inconclusive as it failed to produce a higher-molecular-weight polyether (*Table 2*, entry 4).

A significant drawback of the reactions carried out with caesium carbonate as the base in THF as solvent is the occurrence of C-alkylation. Although the extent of C-alkylation is lower than that observed for polycondensations under classical conditions (*Table 1*), it leads to polymers that are still likely to be branched and that contain several different repeating units (O-alkylated, C-alkylated, and branched unit with both O- and C-alkylation).

In the Williamson synthesis with metal phenoxides the ratio of O- to C-alkylation is known to be affected by factors such as solvent and counterion[18]. In particular the use of conditions that promote complexation of the cation leads to alkylations at the more nucleophilic oxygen site.

The absence of C-alkylation in experiments involving **3** and KF or K_2CO_3 in the presence of 18-crown-6 supports this view. With caesium carbonate, C-alkylation is only avoided when a strongly solvating solvent such as DMF is used. With Cs_2CO_3 in THF, interaction of the metal cation with the phenoxide anion is such that a transition state favouring C-alkylation is preferred. Furthermore, as the molecular weight of the polyether increases, the phenoxide chain end is increasingly surrounded by the non-polar polymer, a factor that would favour C-alkylation.

Polyethers made from the silylated monomer **3** have solubility properties that differ from those of polyethers made from the phenolic monomer **1**. Typically, the polymers that are obtained by the carbonate-initiated polymerization of silylated monomer **3** are soluble in most organic solvents such as tetrahydrofuran, dichloromethane, chloroform and diethyl ether. In contrast, the low-molecular-weight materials obtained from the AB monomer **1** are soluble only in polar solvents such as methanol and dimethylformamide.

The ^1H n.m.r. spectra of various batches of **2** illustrate the differences in the structures of the O-alkylated polymers and the polymers that contain both O- and C-alkylated units (*Figure 1*). For example, the polyethers prepared from **3** in the presence of fluoride ions are O-alkylated (*Figure 1a*). Because the polymer only has a low molecular weight (*Table 2*, entry 3), the benzylic bromide and alcohol methylene end-groups are seen as small signals at 4.45 and 4.55 ppm respectively, clearly separated from the large benzyl ether signal at 5.0 ppm. Calculation of the molecular weight from the ratio of these signals shows that, coincidentally, the molecular weight calculated by end-group analysis is consistent with the $\bar{M}_n$ value obtained by g.p.c. using polystyrene standards. For the higher-molecular-weight polymer ($\bar{M}_w = 290000$) obtained using caesium carbonate as the base (*Figure 1b*), the benzylic region of the ^1H n.m.r. spectra consists of two broad peaks. The methylene protons near 5.0 ppm correspond to the O-alkylated material while those near 4.0 ppm correspond to C-alkylated material. The broad resonances preclude end-group analysis on these higher-molecular-weight polymers, but the extent of C-alkylation can be calculated easily.

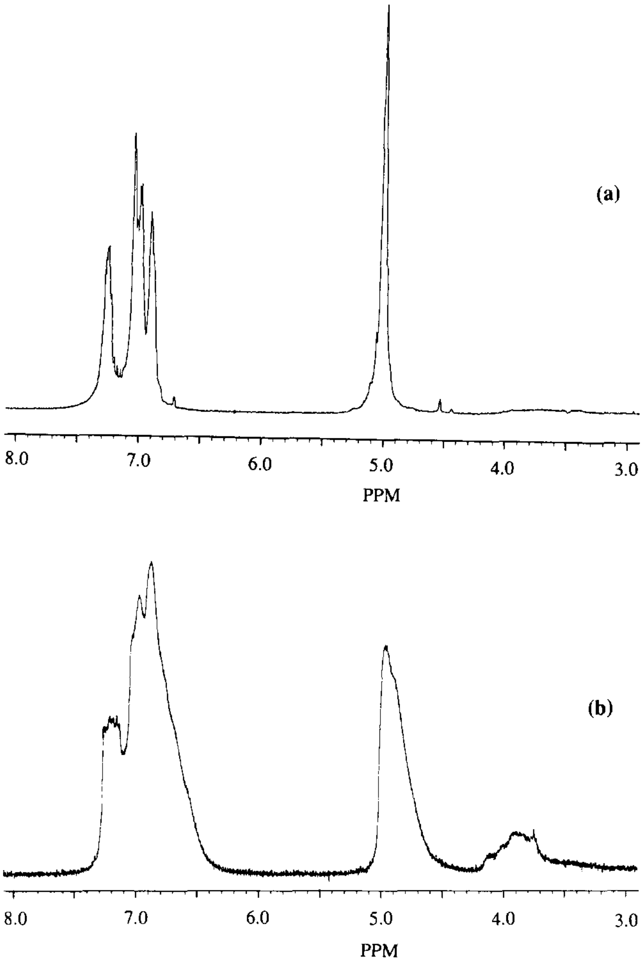
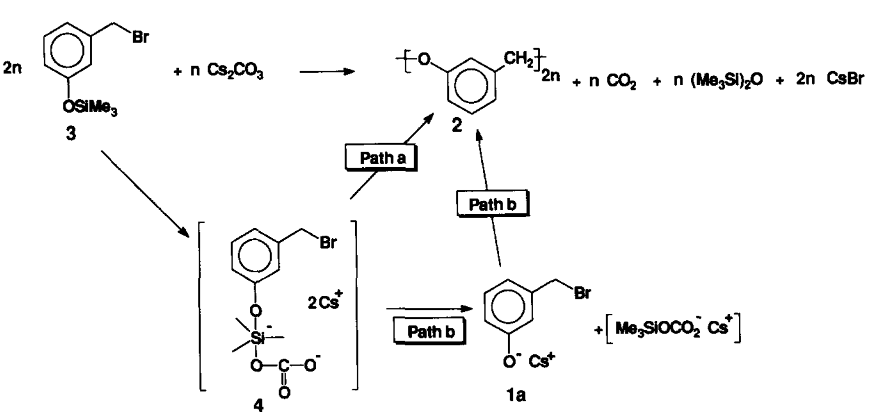


Figure 1 ^1H n.m.r. spectra of polymer **2** prepared in the presence of (a) KF/18-c-6 and (b) Cs_2CO_3

The role of carbonate ion in this polymerization has been investigated. Careful measurement of the stoichiometry of the process indicates that 0.5 mol of carbonate ion is required for each mole of monomer **3** in order to obtain high-molecular-weight polymers. Polymerizations using only 0.06, 0.15, 0.25 and 0.50 mol of caesium carbonate for each mole of **3** were carried out and their progress was monitored by g.p.c. A comparison of the g.p.c. chromatograms of the crude reaction mixtures indicates that the amount of high-molecular-weight polyether, with a low retention volume, is significantly enhanced when the ratio of caesium carbonate to **3** is increased. With a molar ratio of less than 0.5, low-molecular-weight oligomers with higher retention volumes are obtained predominantly. This requirement for a stoichiometric amount of base negates any mechanism in which the carbonate ion is regenerated. This finding is confirmed by the observation that carbon dioxide is evolved during polymerization, and by the results of the model studies described below. *Scheme 2* shows the formation of polymer **2** through intermediate species such as **4** or **1a** in processes that also account for the formation of the end-product CO_2 as well as hexamethyldisiloxane.



Scheme 2

Unfortunately, this polycondensation reaction is not easily applied to the paraisomer, 4-bromomethyltrimethylsilyloxybenzene. During purification, this monomer undergoes a spontaneous condensation reaction. The very high reactivity is due to the facile formation of a benzylic cation that is stabilized by the silyl ether. Self-condensation of such cationic species leads to C-alkylated materials. This is supported by the results of an ^1H n.m.r. study in which only the methylene protons resulting from C-alkylation are observed in the n.m.r. spectra of the soluble fraction of the polymer product.

Model studies of the silicon-assisted etherification

The ether-forming silicon-assisted condensation reaction was investigated further via a model study that involved the condensation of trimethylsilylphenol **5** with benzyl bromide **6** to form benzyl phenyl ether **7**.

The condensation was tested using a variety of nucleophiles and reaction conditions (*Table 3*). In the first series of reactions, fluoride ion was used to promote the condensation. Potassium fluoride and 18-crown-6 afford the product **7** in 96% yield, while a lower yield (71%) is obtained with tetrabutylammonium fluoride.

As can be seen in *Table 3*, high yields of **7** can be obtained with carbonate ions. In DMF, formation of the product was quantitative with caesium carbonate but not with the corresponding potassium or sodium carbonates. In general, the addition of 18-crown-6 to reactions involving potassium carbonate produced high yields of **7** in a variety of solvents such as THF, acetone and acetonitrile. Sodium carbonate is not reactive even with the addition of 15-crown-5. Because caesium carbonate is partially soluble in most organic solvents, the use of a crown ether in combination with Cs_2CO_3 was not necessary.

The etherification reaction also proceeded without side-reaction in the presence of bicarbonate ions. However, the reaction appeared to proceed much slower than with carbonate. Again, the sodium salt was unreactive while caesium bicarbonate was able to promote an effective, if slow, condensation reaction.

Many other activating reagents were examined, such as Lewis acids, sulfates, phosphates, nitrates, hydrides, benzoate, bibenzoate and other oxyanions. Most were ineffective even with added crown ether. One significant exception amongst the oxyanions investigated was potassium silanoate which afforded the desired phenyl benzyl ether **7** in near quantitative yield.

Table 3 Preparation of **7** by condensation of **5** with **6**

Reagent	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)
KF	–	THF	67	3	38
KF	18-c-6	THF	67	41	96
nBu_4NF	–	THF	67	4	71
Na_2CO_3	–	DMF	65	5	26
K_2CO_3	–	DMF	65	15	40
Cs_2CO_3	–	DMF	65	15	99
Na_2CO_3	15-c-5	THF	67	15	0
K_2CO_3	–	THF	67	16	0
K_2CO_3	18-c-6	THF	67	11	95
Rb_2CO_3	–	THF	67	16	72
Rb_2CO_3	18-c-6	THF	67	15	82
Cs_2CO_3	–	THF	67	5	81
K_2CO_3	18-c-6	CH_2Cl_2	40	17	22
K_2CO_3	18-c-6	Acetone	56	17	96
K_2CO_3	18-c-6	CH_3CN	60	17	99
$NaHCO_3$	15-c-5	THF	67	16	0
$KHCO_3$	18-c-6	THF	67	5	29
$CsHCO_3$	–	CH_3CN	60	16	99
$KOSi(CH_3)_3$	–	THF	67	27	98

[a] 1.0 mol of reagent used, except for the bicarbonates (2.0 mol)

Table 4 Stoichiometric relationship between carbonate and **7** in the condensation of **5** with **6** (1 mol of each)

K_2CO_3 (mol)	Yield of 7 (%)
1.00	94
0.50	93
0.27	42
0.12	17
0.05	7

Reactions in THF (67°C, 20 h) with 18-c-6 (0.01 mol)

The role of carbonate in silicon-assisted etherification

The role and fate of carbonate ion in this etherification reaction have also been investigated through the use of the model system. In particular, the stoichiometric relationship between the carbonate ion and the product **7** was studied (*Table 4*). If 1.0 mol or more of K_2CO_3 is added to the system consisting of 1.0 mol of both reagents **5** and **6**, approximately 1.0 mol of the benzyl ether **7** is isolated. With 0.5 mol of K_2CO_3, formation of the benzyl ether is again essentially quantitative. A further decrease in the molar ratio K_2CO_3/**5** (**5** and **6** are used in equimolar amounts) results in a corresponding decrease in the amount of product isolated. Therefore, only 0.5 mol of the difunctional carbonate ion is necessary to obtain 1.0 mol of product **7**.

A similar study with bicarbonate shows that the use of 0.5 mol of caesium bicarbonate with a mole each of **5** and **6**, only leads to a conversion of 48%. At least a full equivalent (1.0 mol) of bicarbonate ion is necessary to approach quantitative formation of the benzyl ether product **7**.

The stoichiometry of the reaction (0.5 mol of carbonate consumed and 0.5 mol of CO_2 evolved per mole of **5**) is confirmed by monitoring the amount of carbon dioxide evolved both gravimetrically (precipitation of $BaCO_3$ from $Ba(OH)_2$) and by volumetric titration.

The amount of carbon dioxide evolved with bicarbonate ion was also monitored. Under the same reaction conditions, the generation of carbon dioxide from reactions involving bicarbonate was a less efficient and much slower process, as only ~0.2 mol of carbon dioxide were generated from 1.0 mol of caesium bicarbonate and 1 mol each of **5** and **6**.

Control experiments using gravimetric analysis to detect the evolution of carbon dioxide were performed to elucidate the exact role of carbonate in the condensation reaction. No carbon dioxide evolution was detected when benzyl bromide and caesium carbonate were used in the absence of trimethylsilylphenol. In contrast, carbon dioxide is produced upon addition of caesium carbonate to trimethylsilyl phenol **5** alone. When either carbonate or bicarbonate ion is added to the silyl ether **5** in the presence of benzyl bromide, carbon dioxide is evolved. These experiments clearly support a process in which carbonate is involved in the initial attack onto the silyl ether **5** to produce an activated species such as **8** that is key to this condensation reaction.

In an attempt to determine whether initial attack of the carbonate ion onto the silyl ether **5** leads to phenoxide anion or a reactive pentacoordinate silicon species, the reaction was monitored by u.v. spectroscopy. The characteristic absorption peak of the phenoxide ion at 300 nm is readily differentiated from the absorption peaks of other components of the system in acetonitrile.

Reagents such as caesium carbonate, caesium bicarbonate, potassium fluoride and potassium silanoate were found to cleave the silyl ether **5** affording a phenoxide anion detectable by u.v. spectroscopy. ^1H n.m.r. monitoring of these experiments confirmed this cleavage with the disappearance of the trimethylsilyl protons of **5** at 0.24 ppm.

Phenoxide anion was also detected when benzyl bromide was present together with **5** in a reaction mixture that contained potassium fluoride or potassium silanoate. In contrast, phenoxide ion was not observed in experiments in which either caesium or potassium carbonate was added to a solution containing both silyl ether **5** and benzyl bromide. Therefore, it appears that in the presence of benzyl bromide, carbonate ions do not produce a concentration of free phenoxide high enough to be detected by this simple u.v. experiment. Consequently, the reaction must proceed through a pathway in which free phenoxide is either not formed, or is consumed as rapidly as it is formed and is not accumulated in the reaction medium.

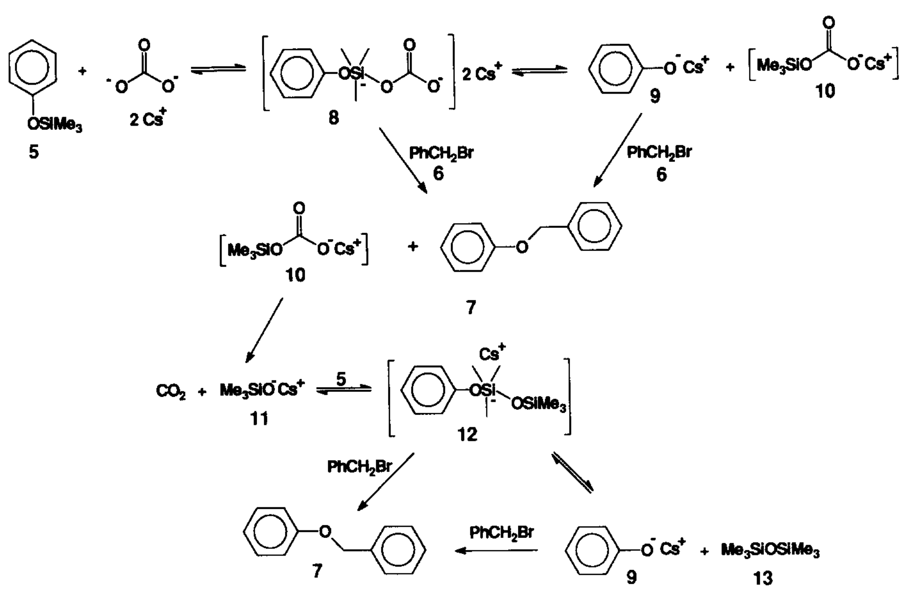
It is interesting to note that no C-alkylation was detected in any of the model reactions involving the trimethylsilylphenol **5** even though a phenoxide anion is known to be generated. To investigate this discrepancy, potassium fluoride was used in a system consisting of 1,3-bis-(trimethylsilyloxy)benzene and benzyl bromide **6**. A full equivalent of crown ether was added in order to increase the concentration of free phenoxide, thereby increasing the likelihood of side-reactions as resorcinol should be more activated to C-alkylation. However, no C-alkylated products were detected and the 1,3-bis(benzyloxy)-benzene was isolated in quantitative yield. These results suggest that the use of a silyl ether in etherification reactions is useful in decreasing the likelihood of C-alkylation side-reactions.

A possible mechanism for the silicon-assisted etherification reaction

A plausible mechanism based on these observations as well as relevant literature can be proposed (*Scheme 2*). The key intermediate is **4** with a pentacoordinate silicon. Direct polycondensation of **4** (path a) leads to polymer **2**, while the alternative route involving the formation of phenolate **1a** (path b) is also possible. Detailed consideration of the model reaction (*Scheme 3*) suggests that the initial step is the nucleophilic attack of the carbonate ion on silyl ether **5** to afford a pentacoordinate silicon species **8**. A similar hypervalent silicon moiety has been proposed as the reactive intermediate in group transfer polymerizations[19]. The additional electron density near the silyl ether oxygen enables the nucleophilic attack of **8** onto the electrophilic benzyl bromide to give the desired product, **7**, and a silylated carbonate, **10**. Alternatively, **8** may release a very small equilibrium concentration of the phenoxide **9** that is immediately consumed by reaction with **6**, and is therefore not detected by u.v. spectroscopy. Reactions carried out with monitoring of the concentrations of reactants **5** and **6** over time by gas chromatography show that the overall reaction rate is not affected by changes in benzyl bromide concentration. Therefore, the rate-determining step must be attack of the carbonate ion on the silyl ether.

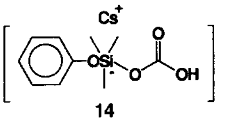
There are at least two possible reaction pathways available to the silylated carbonate ion **10**. In one of these (*Scheme 3*), **10** may decompose to give carbon dioxide and the silanoate anion, **11**. The released silanoate anion can then attack silyl ether **5** to generate **12**. Once again, formation of **7** may then result either from direct attack of **12** onto benzyl bromide or through the intermediate release of a small concentration of the nucleophilic phenoxide **9**, followed by reaction with **6**. The sole silicon-containing end-product of the overall process is hexamethyldisiloxane, **13**.

Alternatively, the silylated carbonate ion, **10**, may attack **5** in an analogous process that would eventually lead to **7** and bis(trimethylsilyl)carbonate. Extrusion of CO_2 from bis(trimethylsilyl)carbonate would produce the observed hexamethyldisiloxane **13**. The extrusion of carbon dioxide by bis(trimethylsilyl)carbonate has been considered earlier[20] in a different context. Because this extrusion occurs at a much higher temperature than used in this reaction, the mechanism proposed in *Scheme 3* is probably preferred.

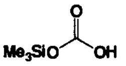


Scheme 3

Monitoring of the reaction by ^{29}Si n.m.r. spectroscopy at 23°C only revealed the presence of two silicon-containing species: the starting material **5** ($\delta = 18$ ppm relative to TMS) and the disiloxane final product **13** ($\delta = 7$ ppm). This finding is not unexpected as the various other silicon-containing moieties shown in *Scheme 3* are not expected to accumulate in this reaction medium. In contrast, the absence of a signal corresponding to bis(trimethylsilyl)carbonate provides further support for the proposed mechanism (*Scheme 3*). Similar observations were made in ^{29}Si n.m.r. experiments at -70°C.



14



15

The bicarbonate-promoted reaction proceeds at a much slower rate than the carbonate-promoted reaction. In analogy to the mechanism shown in *Scheme 3*, reaction of caesium bicarbonate with **5** would proceed via formation of **14**. Reaction of **14** with benzyl bromide affords the desired ether product **7** with silylated bicarbonate **15** as a by-product. Silylated bicarbonate **15** is the conjugate acid of intermediate **10** postulated in *Scheme 3* for the corresponding reaction with caesium carbonate. In the absence of any formal negative charge, **15** is expected to be much less reactive than **10**, hampering its further reaction and leading to its accumulation in the reaction mixture with a much slower evolution of CO_2. Indeed, ^{29}Si n.m.r. monitoring of the bicarbonate-promoted condensation at -70°C allowed the observation of a third silicon-containing species, silylated bicarbonate **15**, as a peak at $\delta = 10$ ppm, in addition to **5** and **13** (*Figure 2*). However, as the reaction reached completion, the resonance at 10 ppm attributed to **15** disappeared, as would be expected for this intermediate.

The ^{29}Si n.m.r. experiments also indicate that no appreciable concentration of silanoate anion **11** is present at any time during the overall process. The silanoate anion is expected to be highly reactive, adding to the silyl ether **5** faster than the carbonate ion does. Because **11** cannot be detected on the n.m.r. time-scale, it is believed that it is not involved in the rate-determining step, being consumed as soon as it is formed. Indirect support for the involvement of a silanoate intermediate is provided by the observation that potassium silanoate quantitatively promotes the condensation reaction between **5** and **6** (*Table 3*) with hexamethyldisiloxane **13** observed as the final silicon-containing product.

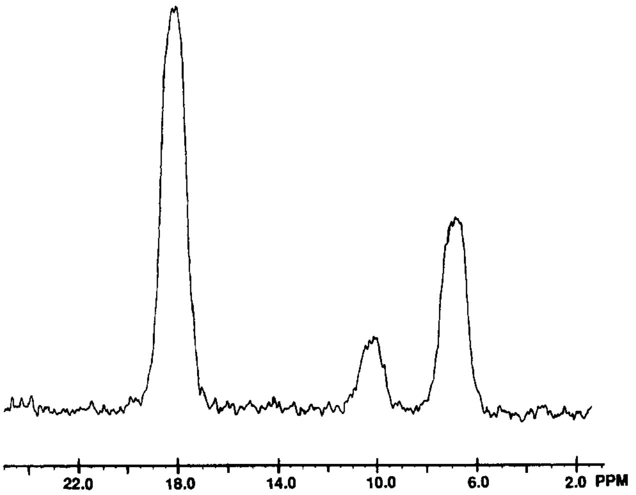


Figure 2 ^{29}Si n.m.r. spectrum recorded at -70°C for the reaction of **5** and **6** in the presence of caesium bicarbonate

CONCLUSION

The condensation of benzyl bromide and trimethylsilyloxybenzene in the presence of carbonate or even bicarbonate ions appears to be a very effective alternative to the classical Williamson synthesis. This reaction is particularly effective in the preparation of high-molecular-weight polymers by polycondensation of an AB-type monomer such as 3-bromomethyl-trimethylsilyloxybenzene. Support for a mechanism involving carbonate attack onto the silicon is provided by several experiments on model compounds. The stoichiometry of the reaction is such that 0.5 mol of carbonate is consumed generating 0.5 mol of carbon dioxide and 0.5 mol of the desired product **7**. The remaining 0.5 mol of product **7** is probably formed from the silanoate ion **11** that is generated *in situ*. U.v. spectroscopy confirms that no appreciable concentration of free phenoxide is present during reaction, while gas chromatography indicates that benzyl bromide is not involved in the rate-determining step. Finally, additional support for the proposed mechanism is provided by the observation of an intermediate by ^{29}Si n.m.r. spectroscopy. In the preparation of high-molecular-weight polymers from 3-bromomethyl-trimethylsilyloxybenzene, the presence of silicon appears to enhance the solubility of the polycondensation products allowing the oligomers to remain in solution, such that further reaction may proceed. Therefore, factors which usually contribute to the formation of low-molecular-weight products under phase-transfer conditions such as precipitation at the oligomer stage, loss of functionality through side-reactions, or crosslinking processes do not appear to affect this polycondensation.

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