Using "Anhydrous" Hydrolysis To Favor Formation of Hexamethylcyclotrisiloxane from Dimethyldichlorosilane

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The reaction between dimethyl sulfoxide and Me_2SiCl_2 leads to the formation of cyclic siloxanes, principally the more highly strained six-membered ring hexamethylcyclotrisiloxane (D_3), via linear α,ω-dichlorosiloxanes. At short reaction times (~15 min), the reaction was shown not to be undergoing equilibration reactions (ligand metathesis) to a significant degree. A mechanism for the formation of D_3 and D_4 (octamethylcyclotetrasiloxane) is proposed that invokes conversion of a chlorosilane group into a sulfonium ion intermediate **12**. The preferential formation of D_3 over D_4 is attributed to the greater steric encumbrance of the activated chain termini ($SiOS^+Me_2$) than in the corresponding hydrolysis reaction (SiOH). Both the chain extension reactions **12** → **3** and cyclization reactions **12** → D_3 are retarded, resulting in a higher selectivity (with DMSO as the oxygen source) for the intramolecular reaction producing D_3 than in the case of hydrolysis. The experimental results are inconsistent with silanone formation.

Introduction

Cyclic siloxanes constitute an important class of silicone polymers because the most practical method for preparing high molecular weight polysiloxanes is the ring-opening polymerization of cyclic monomers.[2] The polymerization of hexamethylcyclotrisiloxane (D_3), with its greater ring strain (12−15 kcal/mol[3]), leads to higher molecular weight polymers with lower molecular weight polydispersity than the analogous polymer produced from octamethylcyclotetrasiloxane (D_4).

The cyclic dimethylsiloxanes D_3, D_4, D_5 (decamethylcyclopentasiloxane), etc., are usually made by the hydrolysis of dichlorodimethylsilane.[4,5] The formation of cyclic oligomers is generally accompanied by substantial (≥50%) amounts of linear dimethylsiloxanes, although their formation can be suppressed by the use of organic (co)solvents for the hydrolysis,[2] particularly diethyl ether.[4] Under normal conditions, D_4 is the major cyclic constituent of the hydrolytic products of Me_2SiCl_2.[6] Thus, the development of a method to produce primarily D_3 would be advantageous.

Sulfoxides have been shown to react with chlorosilanes.[7−9] Thus, Chan and co-workers[10] demonstrated that $HSiCl_3$ reduces dimethyl sulfoxide (DMSO) to dimethyl sulfide. While the fate of the oxygen in this reaction involved Si−O bond formation, the structure of the silicon-containing product was not elucidated. Other related reactions have been noted.[11] For instance, Lappert et al.[12] showed that SiO_2 formation accompanied the reaction of DMSO and $SiCl_4$.

The conversion of chlorosilanes into disiloxanes, using DMSO as the oxygen source, was reported in a French patent in 1965.[13] This reaction has been subsequently rediscovered by Voronkov and co-workers,[14] Weber et al.,[15] and ourselves.[16]

Voronkov and co-workers described the conversion of Me_2SiCl_2 to a mixture of cyclic dimethylsiloxanes; the

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(7) **Previous workers have described explosive reactions between Ph_2SO and $HSiCl_3$.** While no such problems were observed in the many times we have examined the reactions described in this paper, caution must be exercised when attempting these and related reactions.[8]

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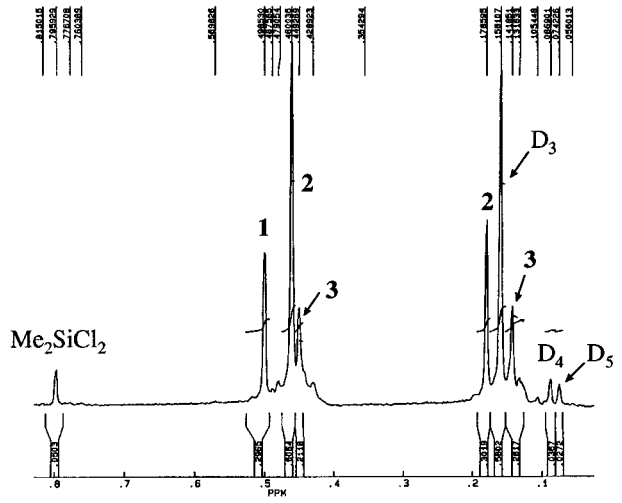


Figure 1. ^{1}H NMR spectra (0−1 ppm) of reaction mixtures of Me_2SiCl_2 and DMSO at 15 min.

product ratio was not disclosed. Weber et al. described the related reaction of Ph_2SiCl_2 with DMSO to give $D_3^{Ph_2}$ (91%) and $D_4^{Ph_2}$ (9%). In both cases, the mechanism proposed to lead to these products involved the cyclotrimerization and cyclotetramerization of $R_2Si{=}O$ (R = Me or Ph, respectively).

We have independently examined this reaction. Given the wide variety of nucleophiles present in the reaction medium, we were skeptical of the involvement of silanones. We have, therefore, probed the mechanism of the reaction in some depth. As importantly, we have found that under the appropriate reaction conditions, the combination of Me_2SiCl_2 and DMSO preferentially leads (>85%) to the formation of D_3 in the absence of linear polymers.

Results and Discussion

Basic Reaction. The reaction between a 1:2 ratio of Me_2SiCl_2 and DMSO in diethyl ether produced an ^{1}H NMR spectrum displaying only a few singlets. The ability to observe base line separation of the signals for most of the reagents, intermediates, and products in the ^{1}H NMR spectrum greatly facilitated the mechanistic study outlined below (Figure 1). The signals were subsequently determined, by comparison with authentic samples, to arise from the α,ω-dichlorosiloxanes ($ClSiMe_2(OSiMe_2)_nCl$) **1** ($n = 1$), **2** ($n = 2$), and **3** ($n = 3$) and D_3 (Scheme 1). Over a short time (typically <30 min), most of these signals collapsed to a clean spectrum containing only 4 peaks arising from D_3, D_4 (occasionally D_5 and higher homologues), and chloromethyl methyl sulfide **4** (2 peaks). The reactions were accompanied by the formation of variable amounts of a crystalline material subsequently identified to be chlorodimethylsulfonium chloride **5** ($Me_2S^+ClCl^-$).[12]

The corresponding reaction of Me_2SiCl_2 with water led to D_3:D_4 ratios containing at least 50% D_4:[6] a typical result in diethyl ether was D_3: D_4: D_5 (30:53:17) after 15 min. Further reaction times led to an increase in D_4 at the expense of D_3. The striking difference between this reaction and the reaction with DMSO in place of water, noted above, was the ratio of D_3/D_4 at the completion of the reaction; with DMSO as the oxygen source, in the optimal case, the product ratio was D_3: D_4: D_5 (74:15:11) (some quantities of **1** and **3** were also present, Figure 1).

Several experiments were attempted in order to establish the nature of the reaction mechanism, particularly in light of the proposition that silanones could be involved,[14,15] and better understand the origin of the preferential formation of D_3. These experiments are described below. In the vast majority of reactions reported, the concentrations of DMSO and Me_2SiCl_2 were held fixed to facilitate comparison between experiments. Snapshots, in the ^{1}H NMR, of the progress of the reactions were always taken at 15 min reaction times: all further discussion, unless otherwise noted, refers to this time period.

Solvent Effects. The reaction between DMSO and Me_2SiCl_2 was examined neat and in the presence of aprotic solvents of differing polarity. The reaction was very sluggish in the absence of solvents. A 1:1 mixture of DMSO and Me_2SiCl_2 was allowed to react for 15 min, at which point the product distribution was determined by ^{1}H NMR. A second aliquot of DMSO was added, and the reaction was allowed to proceed for an additional 15 min. This process, repeated three additional times, led to the reaction profile shown in Figure 2 (Table 1). High conversion (complete loss of Me_2SiCl_2) was only observed at high DMSO concentrations and longer reaction times. It can be further seen that only toward the end of the observation were cyclic oligomers (D_4) beginning to form.

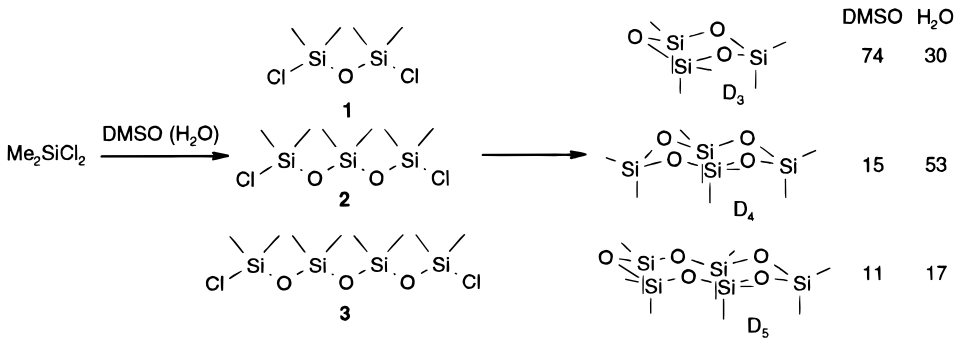
In relatively nonpolar solvents, CCl_4, isopropyl and butyl ether, dioxane and pentane, the reactions were often incomplete after several hours (Table 1, Figure 3). It was immediately clear that polar solvents dramatically, favorably affected the rate of reaction. Thus, the reactions in diethyl ether, acetonitrile, ethyl acetate, and THF were complete within 30 min or less, as was the reaction in xylene. Diethyl ether was found to be the solvent which combined a rapid reaction rate (complete in <20 min) and high D_3:D_4 ratio (maximum 87:13). The remaining experiments examined the details of the reaction in diethyl ether.

Kinetic Profile. The early course of the reaction between DMSO and Me_2SiCl_2 was followed closely to further facilitate an understanding of the mechanistic parameters (Figure 4). A precipitous drop in [Me_2SiCl_2] was accompanied by an increase in the linear siloxane **1**−**3** concentrations. Subsequently, these too were consumed to form D_3 and D_4. It can be seen that, with time, the concentration of D_3 increased at the expense of **2** and D_4 at the expense of **3** (see below).

The D_3:D_4 product ratio was also found to depend on the order of addition. When DMSO was added slowly to Me_2SiCl_2 in diethyl ether, higher D_3:D_4 ratios were observed than when the addition order was reversed (Table 1, entries 20 and 21).

Effect of Dilution. There are clearly two processes occurring in the reaction between Me_2SiCl_2 and DMSO. The first is the oligomerization leading to linear siloxanes $Me_2SiCl_2 \rightarrow$ **1** $\rightarrow$ **2** $\rightarrow$ **3**. The second process involves the cyclization of **2** and **3**, respectively. The unimolecular cyclization reactions **2** $\rightarrow D_3$ (with respect to **2**, see below) are expected to be favored, at lower concentrations of Me_2SiCl_2, over the intermolecular bimolecular chain extension process **2** + $Me_2SiCl_2 \rightarrow$ **3**.

Scheme 1



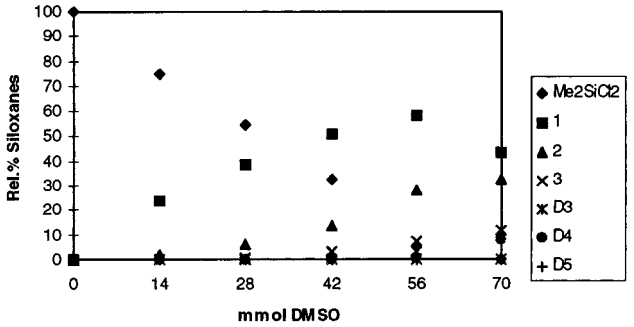


Figure 2. Siloxane distribution in the reaction of DMSO with Me_2SiCl_2 as a function of DMSO concentration.

This was tested by decreasing the concentration of the solution, which should favor the unimolecular cyclization over the bimolecular process. As the initial Me_2SiCl_2 concentration in ether was increased, the proportion of D_3 in the reaction mixture decreased. The benefit of increased D_3 production at high dilution is somewhat offset, in a practical sense, by the necessity to use large volumes of diethyl ether (Figure 5).

Discounting Redistribution under Thermodynamic Control. Silanes possessing reactive groups undergo redistribution (ligand metathesis) reactions.[17−21] The metathesis reaction of halides and siloxy groups usually requires catalysts such as acids,[22,23] quaternary ammonium halides,[24] silicon-selective nucleophiles,[25] organometallic species, or high temperatures.[26,27]

In the reaction with DMSO, two new materials were produced, **4** and **5**. These compounds, as well as the solvent DMSO and the acid byproduct HCl, were examined as potential redistribution catalysts. Neither DMSO, **4**, nor **5** catalyzed the redistribution at a rate comparable to the rate of siloxane formation: the most reactive of these, DMSO, led to a conversion of D_3/D_4 50:50 → 43:57 only over several hours. Thus, on the time scale of the experiment, we conclude that neither **4**, **5**, nor DMSO are effective redistribution catalysts.

The addition of gaseous HCl to the 50:50 D_3/D_4 mixture led to rapid redistribution (10 min) to give a D_3:D_4 ratio of 3:97. This final ratio is very different than that generated in the reaction between Me_2SiCl_2 and DMSO. Thus, HCl, an effective redistribution catalyst[2] in the absence of DMSO, cannot be present in significant quantities in these reactions: where both HCl and DMSO are present, redistribution occurs over several hours. These observations are consistent with HCl being removed from the reaction as it is formed. It is presumably sequestered as the sulfonium salt **5**.

Direct Cyclizations of 1−3 and 6. The initial products of the reaction were shown to be the α,ω-dichlorosiloxanes **1**−**3**. The direct cyclization of each of these compounds with DMSO was attempted to establish if ligand redistribution/metathesis reactions were occurring on the time scale of the cyclic oligomer formation.

The reaction of tetrasiloxane **3** with DMSO or water in Et_2O led primarily to D_4. Disiloxane **1** gave a mixture of **3** and D_4 with either reagent but none of the trisiloxane species **2** and little D_3 (Scheme 2).

It was possible to prepare a small amount of 1,11-dichlorododecamethylhexasiloxane (**6**). The reaction of **6** in ether with DMSO led slowly to D_6 (**7**; dodecamethylcyclohexasiloxane). After longer reaction times (overnight), there was still no D_3; the amount of D_4 produced was <2%. This provides additional support for the postulate that redistribution is not an important mechanism under these conditions.

When trisiloxane **2** was reacted in diethyl ether with DMSO or water, respectively, the predominant silicon-containing product (>95%) of the reaction was D_3. This suggests that the challenge of producing D_3 is reduced to the selective synthesis of **2**. Preparing large quantities of **2** exclusively, however, is a rather difficult task: the maximum yield of **2** from Me_2SiCl_2 using water or DMSO that we were able to obtain was about 15% (of the silicon-containing species).

Condensation reactions between **1** or **2** and DMSO in the presence of D_3 or D_4 were undertaken to deter-

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Table 1. Product Distributions in the Production of α,ω-Dichlorosiloxanes and Cyclic Siloxanes

entry	conditions[a]	Me_2SiCl_2	**1**	**2**	**3**	D_3	D_4	$D_5 + D_6$
1	2 H_2O:3 Me_2SiCl_2, 3 h	47	7	5	10	2	21	9
2	neat DMSO (1 equiv), 15 min	75	24	2	0	0	0	0
3	neat DMSO (2 equiv), 30 min	55	39	6	1	0	0	0
4	neat DMSO (3 equiv), 45 min	33	51	13	3	0	0	0
5	neat DMSO (4 equiv), 60 min	5	59	28	7	0	1	0
6	neat DMSO (5 equiv), 75 min	0	43	32	12	0	8	0
7	2 DMSO:1 Me_2SiCl_2, CCl4, 1 h	7	54	21	7	9	2	0
8	2 DMSO:1 Me_2SiCl_2, pentane, 1 h	63	21	5	5	6	2	
9	2 DMSO:1 Me_2SiCl_2, dibutyl ether, 3 h	17	42	18	4	14	6	
10	2 DMSO:1 Me_2SiCl_2, diisopropyl ether, 2 h	17	30	31	4	15	3	
11	2 DMSO:1 Me_2SiCl_2, CH3CN, 30 min	0	7	5	9	13	43	24
12	2 DMSO:1 Me_2SiCl_2, xylene, 15 min	0	4	6	5	44	36	5
13	2 DMSO:1 Me_2SiCl_2, THF, 1 h	0	5	3	2	48	36	7
14	2 DMSO:1 Me_2SiCl_2, EtOAc, 3 h	0	10	15	8	20	30	17
15	DMSO:1 Me_2SiCl_2, Et_2O, 5 mL, 15 min	0	16	9	7	40	27	2
16	2 DMSO:1 Me_2SiCl_2, Et_2O, 20 mL, 15 min	0	26	9	8	43	13	0
17	2 DMSO:1 Me_2SiCl_2, Et_2O, 50 mL, 15 min	0	23	0	14	50	11	3
18	2 DMSO:1 Me_2SiCl_2, Et_2O, 100 mL, 15 min	0	18	0	16	54	9	2
19	2 DMSO:1 Me_2SiCl_2, Et_2O, 200 mL, 15 min	0	8	0	10	60	14	7
20	2 DMSO:1 Me_2SiCl_2, Et_2O, 20 mL, 15 min; order of addition: DMSO to Me_2SiCl_2	0	6	0	8	75	8	2
21	2 DMSO:1 Me_2SiCl_2, Et_2O, 20 mL, 15 min; order of addition: Me_2SiCl_2 to DMSO	0	14	0	4	50	21	6

[a] Reaction time: 3 h.

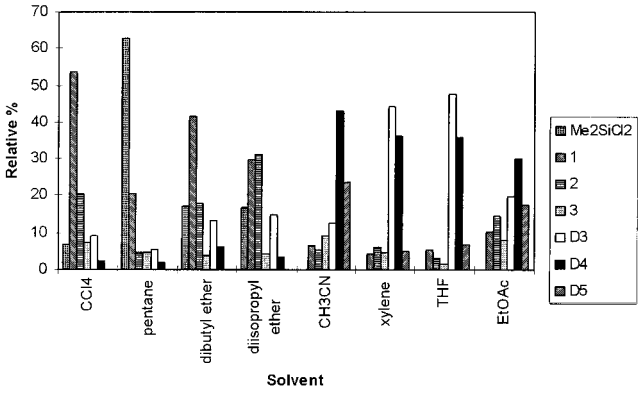


Figure 3. Distribution of linear and cyclic siloxanes formed from DMSO and Me_2SiCl_2 in different solvents.

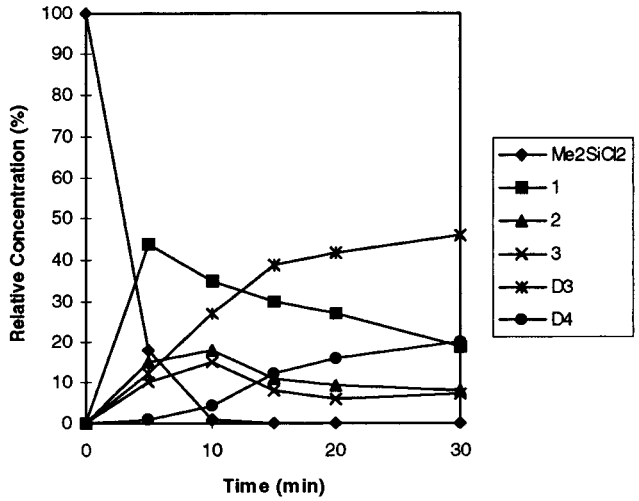


Figure 4. Evolution of siloxanes from DMSO and Me_2SiCl_2 in diethyl ether.

mine if the conversion of the linear chlorosiloxanes to cyclic siloxanes was accompanied by conversion of D_3 to D_4 or vice versa. The reaction of **1** with DMSO and D_4 led primarily to D_4, suggesting direct conversion of **1** → **3** → D_4: little D_3 was observed. The reaction of **1** with DMSO in the presence of D_3 led mostly to **1** → **3** → D_4; the D_3 concentration changed little. Analogous results were observed with **2**. **2** (+ D_3 + DMSO) was converted to D_3 without formation of D_4; **2** (+ D_4 + DMSO) gave D_3 without changing the D_4 concentration (Scheme 2).

The absence of significant ligand redistribution/metathesis reactions of D_3 or D_4 in the presence of HCl + DMSO, DMSO, **4** or **5**, or in the presence of the α,ω-dichlorosiloxanes, within the time frame of the experiments (<1 h), leads us to conclude that the reactions leading to linear and cyclic oligomers in the presence of DMSO are occurring under kinetic control.

Competition Reactions. The relative rates of some of the sequential reactions involved in the conversion of Me_2SiCl_2 to cyclic siloxanes were established by allowing mixtures of **1**−**3** to react with DMSO and following the reactions by ^1H NMR. The competition reaction between a 1:1 mixture of **1** and **2** for DMSO showed very little change in the concentration of **1**; the small decrease in [**1**] was accompanied by the formation of a small amount of **3**. The major change was the loss of **2** with concomitant formation of D_3 (**1**:**2** (50:50) → **1**:**2**:**3**:D_3:D_4 (46:21:9:24:0 (not detected))). Thus, cyclization of **2** → D_3 is faster than bimolecular condensation between **1** + **1** or **1** + **2**. By contrast, under identical conditions with H_2O as the oxygen source, the product ratio was **1**:**2**:**3**:D_3:D_4 (20:33:22:20:5). Thus, the rate ratio of (linear condensation)/(cyclization) is higher with water than with DMSO.

The analogous competitive cyclization between **2** and **3** similarly showed a dependence on the oxygen source. A 1:1 mixture of **2** and **3** led to the mixtures **1**:**2**:**3**:D_3:D_4 (4:22:38:24:12) with DMSO but to **1**:**2**:**3**:D_3:D_4 (3:13:32:24:28) with water. In both cases, the relative rates of cyclic oligomer formation are more favorable to D_3 production: k(**2** → D_3)/k(**3** → D_4) > 1. However, with water, but not with DMSO, there is the additional redistribution of D_3 → D_4, presumably caused by HCl, which depletes D_3 at a competitive rate to cyclization.

Cyclization versus Linear Extension: Effect of Additional Me_2SiCl_2. The relative rates of cyclization versus chain extension were established by examining the efficacy of cyclization of **2** to D_3 in the presence of varying amounts of Me_2SiCl_2. As the initial ratio of

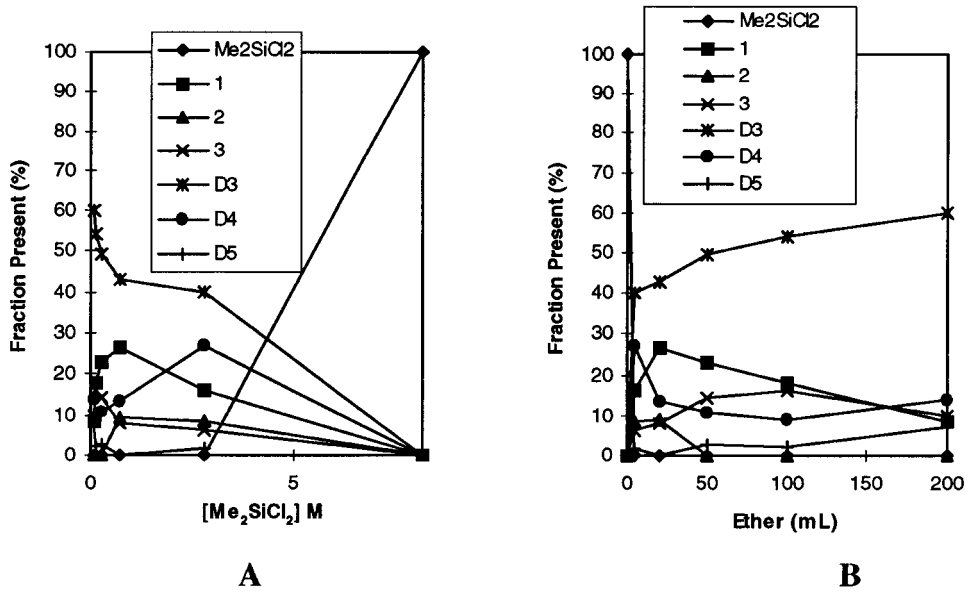
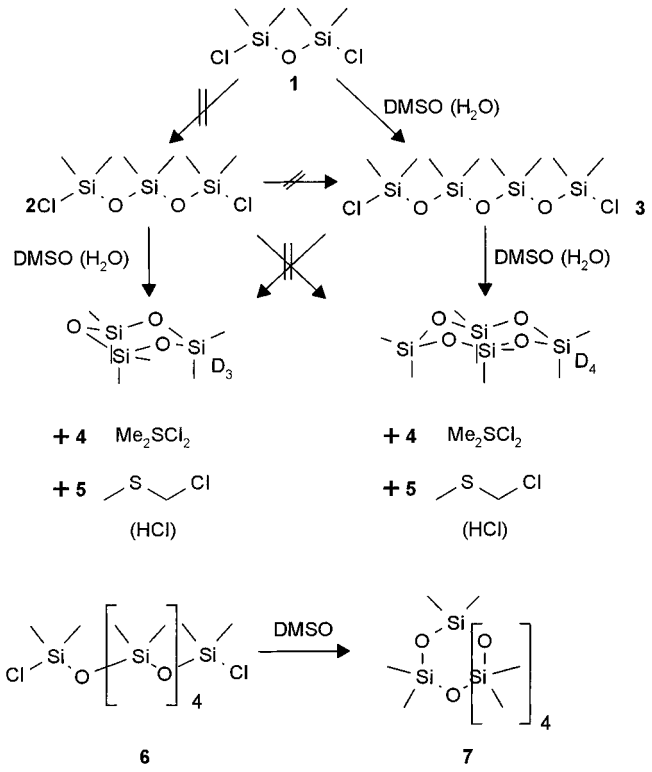


Figure 5. Effect of concentration on the D_3/D_4 ratio: (A) as a function of $[Me_2SiCl_2]$; (B) as a function of Et_2O volume.

Scheme 2



$[Me_2SiCl_2]/[\mathbf{2}]$ increased from 0.0 to 1.5, the product ratio $\mathbf{3}/D_3$ dramatically increased (Figure 6), indicating that the bimolecular chain extension process is competitive with cyclization at higher Me_2SiCl_2 concentrations.

The Proposed Mechanism. Sulfur-Containing Products. Prior to discussing the mechanism of siloxane formation in the presence of DMSO, it is appropriate to comment on the structures of the sulfur-containing products. The formation of **5** arises from the reaction of DMSO with HCl and is accompanied by the production of water (Scheme 3, D).[12] The other sulfur-based product was chloromethyl methyl sulfide (**4**), a compound whose production has previously been described in related reactions (Scheme 3, C).[12,28] Its

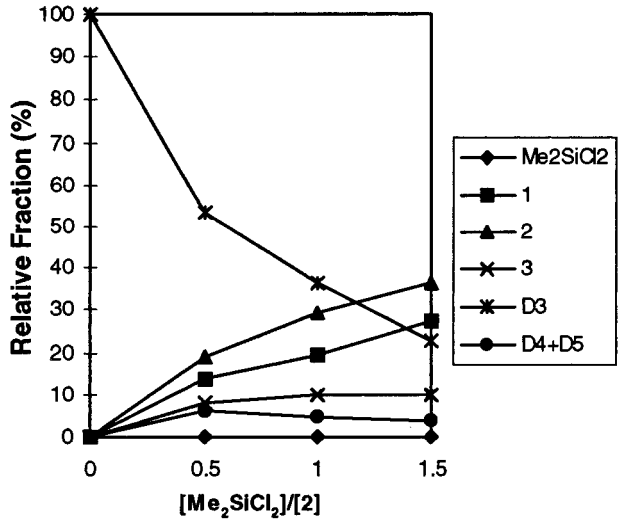


Figure 6. Formation of D_3 from **2** as a function of starting Me_2SiCl_2 concentration.

formation likely involves intermediate **8**, analogues of which have previously been described in Pummerer rearrangements[29] and redox reactions using a chlorosilane/sulfoxide system.[30] Similar intermediates are inferred or known in a variety of alcohol oxidation procedures (e.g., Swern) using DMSO (Scheme 3, A).[28] The decomposition of **8** could lead directly to **1** + **5** or to **4** and the silicone precursor **9**.[31] Although **8** could, in principle, decompose through a sila-Pummerer rearrangement (Scheme 3, B), this was not observed.

Stepwise Progression of the Reaction. In the reaction between Me_2SiCl_2 and DMSO, the DMSO may

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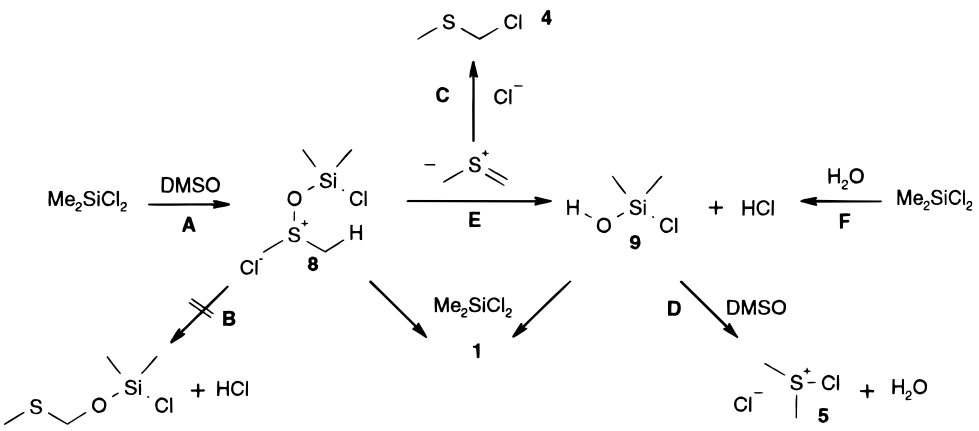
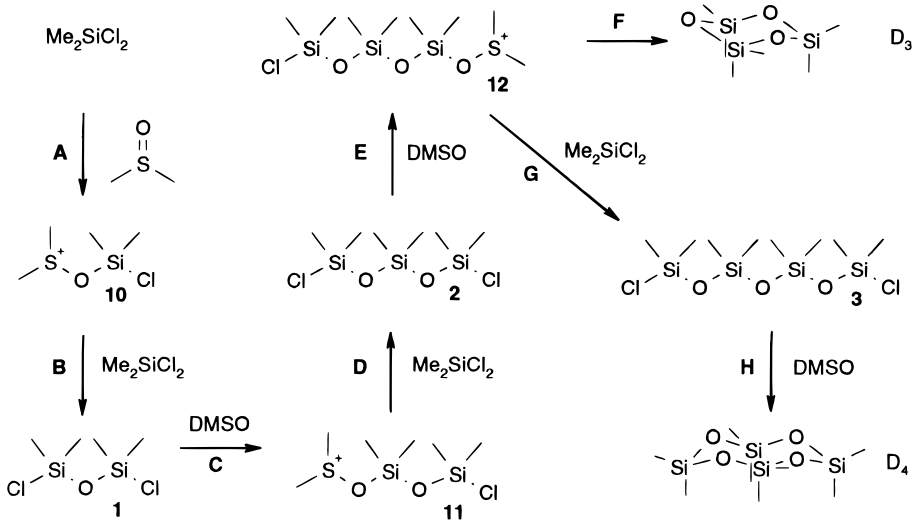
Scheme 3



Scheme 4



serve as a source of oxygen in two ways: (i) as a source of H_2O (Scheme 3, D) and (ii) as an end group from which a nucleophile is generated. The rate of these reactions is clearly accelerated by polar solvents, suggesting polar intermediates (Figure 3).

The progression of the reaction is rather obvious from the evolution of species, as shown in Figure 4. Starting from Me_2SiCl_2, the first observed products are the linear siloxanes in order, **1** → **2** → **3**. Thus, one important sequence in the presence of DMSO involves homologous linear chain extension. A mechanistic proposal for cyclic siloxane formation involves deviation from the linear homologation once the chain reaches the minimum practical length for cyclization (i.e., the six atoms in **2**, D_2 is a highly energetic species[32]), **2** → D_3 and **3** → D_4 (Scheme 4, A−C).

In these events, we believe that a relatively bulky Me_2S^+O group is the reactive terminus of the linear chain **10**−**12** (Scheme 4). As noted above, such intermediates are commonly invoked in DMSO-mediated oxidations. Liberation of the sulfur could be induced during unimolecular cyclization (Scheme 5, A) or, more likely, with concomitant attack by chloride (Scheme 5, B).[33] These two pathways account for both sulfur-containing products **4** and **5** that, however, may also arise from different reactions (Scheme 3).

Thus, conversion of **2** to an activated-species sulfonium ion **12** (Scheme 4, E) is followed by a competition between chain extension with Me_2SiCl_2 giving **3** (Scheme 4, G) or the favored intramolecular cyclization to D_3 (Scheme 4, F). The presence of the bulky group at the chain termini should engender larger steric interactions upon reaction both intermolecularly with Me_2SiCl_2 or intramolecularly. By slowing down both reactions, the natural preference for the intramolecular reaction (higher local concentration, fewer degrees of freedom) over the intermolecular condensation is amplified. This is particularly true at lower concentrations of Me_2SiCl_2. Such a proposal also explains the even higher D_3 selectivity in the case of cyclization of Ph_2SiCl_2. The analogous, but more hindered, compound $ROSiPh_2OS^+Me_2$ will react more slowly and selectively than **12** in an intramolecular fashion to give $D_3^{Ph_2}$ in high yield (91%).[15]

One must account for the difference in D_3/D_4 formation when water and DMSO are used as the oxygen source. The rates of linear chain extension with DMSO were found to be slower than cyclization for the reactions: the rates for **1** + **1** → **3** and **1** + **2** → 1,9-

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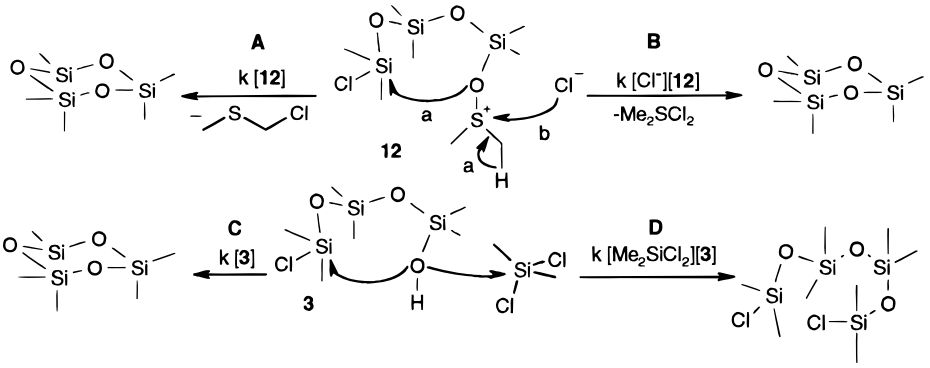
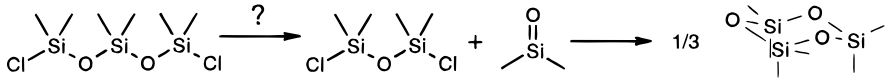
Scheme 5



Scheme 6



dichlorodecamethylpentasiloxane were slower than cyclization **2** → D_3. However, the reaction **2** → D_3 is competitive with linear extension of **2** + Me_2SiCl_2 → **3** (Figure 6). Overall, except at high [Me_2SiCl_2], these factors favor D_3 formation. With water as the oxygen source, the rates of linear extension **1** + **1** → **3** are comparable to cyclization **2** → D_3. Linear extension **2** → **3** by Me_2SiCl_2 might be expected to be even faster. This is likely a consequence of both the reduced steric hindrance at the nucleophilic oxygen and the ability of the hydroxyl group to attack the chlorosilane (Scheme 5, C,D) without the requirement for intervention by an additional nucleophile such as chloride (Scheme 5, B).

Another important difference between the water- and DMSO-initiated reactions is the presence of HCl, a potent redistribution catalyst in the former case. Gaseous HCl led to immediate redistribution favoring D_4 (D_3 + D_4 (1:1) + HCl(g) → D_3 + D_4 (3:97)). It should similarly facilitate redistribution in all the reactions. By contrast, with DMSO as the oxygen source, HCl is sequestered as **5**.

The Question of Silanone Involvement. No role is given to silanones, the intermediates favored by Voronkov[14] and Weber,[15] in the mechanistic suggestions made above. The bulk of the present knowledge of silanone properties[34] originates primarily from studies on transients,[35] although silanones have been observed in argon matrices.[36] The intermediacy of free silanones has been proposed for many reactions which primarily involve gas-phase, high-temperature conditions[37−43] but has been questioned in some of these processes.[44] Much of the evidence for silanone formation is inferred from the presence of small silicone cyclics in reaction mixtures,[45−52] as in the reaction between DMSO and R_2SiCl_2.[14,15]

Silanones have been calculated to be exceptionally reactive toward nucleophilic attack. The addition of water was calculated to be essentially without barrier and with a ΔH of −73 kcal/mol.[53] In the highly polar media in the reactions described above, it seems unlikely that the lifetime of the silanone would be sufficient to allow it to undergo oligomerization prior to interception by one of the many types of nucleophiles present in solution (Cl^-, H_2O, R_3SiOH, DMSO, $MeSCH_2$-Cl, etc.).

There is further data, from the experiments described above, that is inconsistent with the intermediacy of silanones. First, α,ω-dichlorosiloxanes **2** and **3** were converted by DMSO directly to cyclic siloxanes D_3 and D_4 (Scheme 2). It seems unlikely that dimethylsilanone could be involved is such a process, which would involve a depolymerization to form silanones followed by reoligomerization (Scheme 6). If the cyclization can occur without silanone intervention, it is difficult to see why linear homologation cannot proceed similarly without silanones. Second, we have observed that the unimolecular (first order in **2**, see above) cyclization reaction of **2** → D_3 is competitive with the second-order linear extension of **2** + Me_2SiCl_2 → **3** and that formation of **1** from Me_2SiCl_2 is faster than the cyclization of **2** (Figure 6).

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In the reaction mixture of Me_2SiCl_2 and **2**, highly reactive $Me_2Si{=}O$, if formed from Me_2SiCl_2, should competitively oligomerize and insert into **2** giving **3** (and D_3 giving D_4). That is, one would expect much higher product concentrations of **3** and D_4 as a result of these reactions than were observed (Figure 6). In fact, the distribution of linear and cyclic siloxanes originating from Me_2SiCl_2 and the cyclization process of **2** giving D_3 may be more readily explained as the sum of two relatively independent processes: **2** → D_3 and Me_2SiCl_2 → linear + cyclic siloxanes.

Experimental Section

Instrumentation. The ^{1}H NMR spectra were recorded on a Bruker AM-500 (at 500 MHz for protons) spectrometer or Bruker AC-200 (at 200 MHz for protons) spectrometer. ^{13}C and ^{29}Si NMR were performed on a Bruker AC-200 (at 50.3 MHz for carbon) and Bruker AC-300 (at 59.6 MHz for carbon and 59.6 MHz for silicon). Chemical shifts are reported with respect to tetramethylsilane, as the standard, set to 0 ppm.

Preparation of 1−3 and 6. The linear α,ω-dichlorosiloxanes **1**−**3** were initially isolated by careful distillation from an old bottle of Me_2SiCl_2. They are readily prepared in acceptable yield by the method of Patnode and Wilcock,[5] the method that was used to generate hexasiloxane **6** (1,11-dichlorododecamethylhexasiloxane, bp 161 °C at 20 mmHg, lit.[5] 245 °C). **1**−**3** are also commercially available.

1: ^{1}H NMR ($CDCl_3$) δ 0.47 (s, 12H).

2: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 6H), 0.43 (s, 12H).

3: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 12H), 0.41 (s, 12H).

6: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 12H), 0.13 (s, 12H), 0.43 (s, 12H).

For comparison, the ^{1}H NMR chemical shifts of the related cyclic siloxanes and other materials including $ClCH_2SMe$ are provided. D_3 0.15; D_4 0.08; D_5 0.06; D_6 0.077; $ClCH_2SMe$ (**4**) 2.18 (s, 3H), 4.61 (s, 2H); **5** 3.13.

Preparation of D_3/D_4 from Me_2SiCl_2 with H_2O. To a solution of Me_2SiCl_2 (1.7 mL, 14 mmol) in diethyl ether (50 mL) was added H_2O (0.5 mL, 28 mmol). After 15 min, the ^{1}H NMR showed a mixture of D_3:D_4:D_5 (30:53:17) (Table 1, entry 1). Only small quantities of starting and other materials were observed (<2%).

Siloxanes from Me_2SiCl_2 and DMSO in the Absence of Solvents. To Me_2SiCl_2 (8.49 mL, 70 mmol) was added DMSO (1.0 mL, 14 mmol). The ^{1}H NMR was taken after 15 min. To the reaction mixture was added a second aliquot of DMSO (1.0 mL, 14 mmol). This process was repeated a further 3 times (Figure 2, Table 1, entries 2−6).

General Procedure I: Siloxanes from Me_2SiCl_2 and DMSO in Different Solvents. To a solution of Me_2SiCl_2 (1.7 mL, 14 mmol) in solvent (20 mL) was added DMSO (2 mL, 28 mmol). The mixture was stirred at ambient temperature. ^{1}H NMR spectra were generally obtained at 15 min. However, in some cases, reaction was too slow and longer reaction times were utilized (Table 1, entries 7−14, Figure 3).

Product Distributions in Ether. General procedure I was used to prepare the siloxanes in Et_2O. A high ratio of D_3:D_4 was obtained (87:13). Therefore, detailed investigation of the reaction in this solvent was undertaken. The kinetics of the process were followed over several hours. The results are shown in Figure 4.

Dilution Effects. The effect of concentration was probed in the reaction by holding the DMSO:Me_2SiCl_2 ratio constant and varying the dilution volume of ether (Figure 5, Table 1, Entries 15−19): DMSO (2 mL, 28 mmol), Me_2SiCl_2 (1.7 mL, 14 mmol).

Effect of Order of Addition of Me_2SiCl_2 to DMSO. To a solution of DMSO (2.0 mL, 28 mmol) in Et_2O (40 mL) was added Me_2SiCl_2 (1.7 mL, 14 mmol), dropwise. After 1 h, ^{1}H NMR showed the distribution of the reaction products strongly favored D_3. By contrast, the identical reagents, but with the reverse order of reagent addition, led to diminished D_3 production (Table 1, entries 20 and 21).

Redistribution Reactions in the Presence of DMSO, 4, 5, and HCl. A 50:50 mixture of D_3:D_4 (5.6 g, 28 mmol (D_3); 8.3 g, 28 mmol (D_4)) was dissolved in diethyl ether (30 mL). In separate reactions, each of the following reagents was added to the D_3/D_4 mixture and the course of redistribution was followed over time by ^{1}H NMR.

4 (0.27 g, 2.8 mmol): 4 h, D_3/D_4 (50:50).

5 (0.38 g, 2.8 mmol): 2 h, D_3/D_4 (48:52).

DMSO (0.4 mL, 5.6 mmol): 20 min, D_3/D_4 (45:55); 18 h, D_3/D_4 (43:57).

HCl(g): 10 min, D_3/D_4 (3:97).

Redistribution Reactions between Cyclic and Linear Siloxanes. The reaction of D_3 or D_4 with **1**, **2**, or **3** in the presence of DMSO allows one to establish the relative rates of redistribution of the cyclic siloxane under these conditions.

D_3 (1.57 g, 7.06 mmol), **1** (1.38 mL, 7.06 mmol), and DMSO (1 mL, 14 mmol) were allowed to react in Et_2O (20 mL). After 15 min, the ^{1}H NMR spectrum showed a ratio of **1**:**2**:**3**:D_3:D_4 (10:0:3:66:21).

D_3 (1.57 g, 7.06 mmol), **2** (1.94 mL, 7 mmol), and DMSO (1 mL, 14 mmol) were allowed to react in Et_2O (20 mL). After 15 min, the ^{1}H NMR spectrum showed only D_3.

D_4 (2.2 mL, 7 mmol), **1** (1.37 mL, 7 mmol), and DMSO (1 mL, 14 mmol) were allowed to react in Et_2O (20 mL). After 15 min, the ^{1}H NMR spectrum showed ratio of **1**:**2**:**3**:D_3:D_4 (12:0:5:2:80). Essentially no D_3 was formed in this process. The proportions indicated the direct conversion of **1** to D_4.

D_4 (2.2 mL, 7 mmol), **2** (1.94 mL, 7 mmol), and DMSO (1 mL, 14 mmol) were allowed to react in Et_2O (20 mL). After 15 min, the ^{1}H NMR spectrum showed a ratio of **1**:**2**:**3**:D_3:D_4 (2:4:0:44:51). The proportions indicated the direct conversion of **2** to D_3 without the participation of D_4.

Cyclization Reactions of 1−3 and 6. To disiloxane **1** (2.7 mL, 14.0 mmol) was added DMSO (2 mL, 28 mmol) in ether (20 mL). After 30 min, the ^{1}H NMR spectrum showed a ratio of **1**:**3**:D_3:D_4 (29:18:17:36) (the major siloxane products >95%).

To disiloxane **1** (2.7 mL, 14.0 mmol) was added H_2O (1 mL, 55 mmol) at room temperature in Et_2O (mL). After 60 min, the ^{1}H NMR spectrum showed a ratio of D_3:D_4:D_5 (11:74:15) (the only siloxane products). D_3 and **2** were present in <1% in the product mixture.

To trisiloxane **2** (1.9 mL, 7.0 mmol) was added DMSO (1.0 mL, 14.0 mmol) at room temperature in Et_2O (10 mL). After 15 min, the ^{1}H NMR spectrum showed a ratio of D_3:D_4 (the major products >95%) to be 86:14. This ratio was unchanged after 1 h!

To trisiloxane **2** (1.9 mL, 7.0 mmol) was added water (0.26 g, 14.0 mmol) at room temperature in Et_2O (10 mL). After 15 min, the ^{1}H NMR spectrum showed a ratio of **2**:D_3:D_4 (8:88:4) (the major products >95%). This ratio was unchanged after 1 night!

To disiloxane **3** (1.21 mL, 3.5 mmol) was added DMSO (0.5 mL, 7 mmol) in ether (10 mL). After 30 min, the ^{1}H NMR spectrum showed a ratio of D_3:D_4 (12:88) (the major siloxane products >95%).

To 1,11-Dichlorododecamethylhexasiloxane **6** (1 mL, 2 mmol) was added DMSO (2 equiv, 285 mL, 4 mmol) in diethyl ether (5 mL). After 15 min at room temperature, the ^{1}H NMR spectrum showed a ratio of 58% starting material and 40% D_6, 0.077 ppm. Other siloxanes were present in very small amounts (<5%).

Competitive Cyclization/Linear Extension of 1−3 in the Presence of Me_2SiCl_2. The relative rate of chain extension versus cyclization was gauged by the competitive reaction of **2** with Me_2SiCl_2.

General procedure I was implemented for the cohydrolysis of **2** and Me_2SiCl_2. The concentration of **2** (1.9 mL, 7.0 mmol)

Table 2. Siloxane Production from 2 as a Function of Me_2SiCl_2 in the Reaction Mixture

Me_2SiCl_2 (equiv)	**1**	**2**	**3**	D_3	$D_4 + D_5$
0	0	0	0	100	0
0.5	14	19	8	53	6
1	20	29	10	37	5
1.5	28	36	10	23	4

and DMSO (1.0 mL, 14.0 mmol) and the volume of diethyl ether (10 mL) were held constant. The number of equivalents of Me_2SiCl_2 was varied from 0−2 in 0.5 equiv increments (1.7 mL, 14 mmol/equiv). The data after 15 min is shown in Table 2 and Figure 6.

Competitive Dimerization of 1 versus Cyclization of 2. To a mixture of **1** (1.38 mL, 7 mmol) and **2** (1.8 mL, 7 mmol) in diethyl ether (20 mL) was added DMSO (0.5 mL, 7 mmol). After 15 min, the distribution of products was **1**:**2**:**3**:D_3:D_4 (46:21:9:24:0).

To a mixture of **1** (1.38 mL, 7 mmol) and **2** (1.8 mL, 7 mmol) in diethyl ether (20 mL) was added H_2O (0.13 mL, 7 mmol). After 15 min, the distribution of products was **1**:**2**:**3**:D_3:D_4 (20:33:22:20:5).

Competitive Cyclization of 2 and 3. To a mixture of **3** (2.43 mL, 7 mmol) and **2** (1.8 mL, 7 mmol) in diethyl ether (20 mL) was added DMSO (0.5 mL, 7 mmol). After 15 min, the distribution of products was **1**:**2**:**3**:D_3:D_4 (4:22:38:24:12).

To a mixture of **3** (2.43 mL, 7 mmol) and **2** (1.8 mL, 7 mmol) in diethyl ether (20 mL) was added H_2O (0.13 mL, 7 mmol). After 15 min, the distribution of products was **1**:**2**:**3**:D_3:D_4 (3:13:32:24:28).

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