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Interconversions among α-(Trimethylsilyl)alkoxides, α-Trimethylsiloxy Carbanions, and Carbonyl Compounds Accompanied by the Trimethylsilyl Anion

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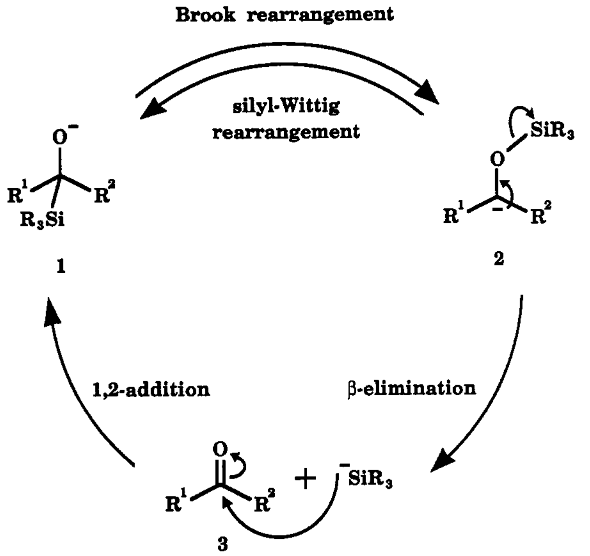
The possible existence of an unusual cycle was investigated, which involved an equilibrium among α-silylalkoxides, α-siloxy carbanions, and carbonyl compounds accompanied by $^-SiR_3$. This postulation was supported by the product distributions of a series of control reactions: the C-deprotonation of 3-methoxybenzyl trimethylsilyl ether, the O-deprotonation of 3-methoxy-α-(trimethylsilyl)benzyl alcohol, and the 1,2-addition of 3-methoxybenzaldehyde with $LiSiMe_3$. Consistent with this postulation were results from the reaction of 3-methoxybenzyl alcohol with KH and $Me_3SiSiMe_3$, giving 3-methoxybenzaldehyde (20% yield), and the reaction of α-cyclopropylbenzyl trimethylsilyl ether with $LiSiMe_3$, affording cyclopropyl phenyl ketone (90% yield).

Introduction

Addition of silylmetallic compounds to an aldehyde or ketone produces α-silylalkoxides (Scheme 1; $3 + {}^-SiR_3 \rightarrow 1$).[1] Most of these alkoxides resulting from aliphatic carbonyl compounds would lead to the corresponding α-silylcarbinols upon aqueous workup.[2,3] Some α-silyl benzylic alkoxides, however, undergo the Brook rearrangement[4] to afford α-siloxy carbanions (i.e., 1 → 2).[5,6] In a special reaction, an α-trimethylsilyl allylic alcohol was reacted with BuLi at −40 °C to give a β-trimethylsilyl ketone.[7] In addition, α-cyclopropylbenzyl alcohol can be converted to γ-(trimethylsilyl)butyrophenone upon silylation with hexamethyldisilane under basic conditions.[8] In these chemical processes, various factors cause the transposition of the silyl group. We attempted to obtain information in support of the novel cycle shown in Scheme 1, in which transposition of a silyl group occurs among α-silylalkoxides, α-siloxy carbanions, and a mixture of carbonyl compounds and $^-SiR_3$.

Scheme 1



To gain an insight into what may cause the oxidation of some silyl-containing species to carbonyl compounds, we treated trimethylsilyl ethers with a base to give the corresponding α-siloxy carbanions. They underwent a β-elimination to give a carbonyl compound and a trimethylsilyl anion. The results from our control experiments provided evidence to support the mechanism shown in Scheme 1, which involves an unusual cycle.

Results

Oxidation of a Benzyl Alcohol and a Benzyl Silyl Ether to the Corresponding Carbonyl Compounds. While envisioning an unusual pathway that may lead a benzyl alcohol to the corresponding aldehyde via a silyl ether intermediate, we treated 3-methoxybenzyl alcohol (4) with $Me_3SiSiMe_3$ (1.2 equiv) and KH (1.0 equiv) in a mixture of THF and HMPA for 55 h (Scheme 2). Aldehyde 5 was isolated in 20% yield. In addition, we allowed benzyl silyl ether 6 to react with a slight excess of $LiSiMe_3$ in HMPA at room temperature. The corresponding ketone 7 was obtained in 90% yield.

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[⊛] Abstract published in *Advance ACS Abstracts,* May 1, 1994.

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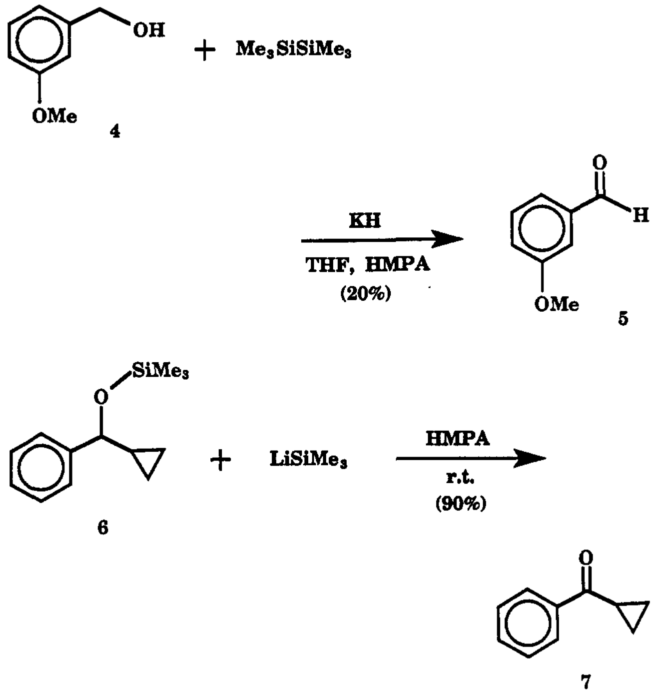
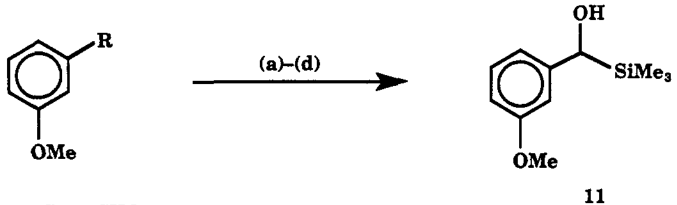
Scheme 2



Scheme 3ᵃ

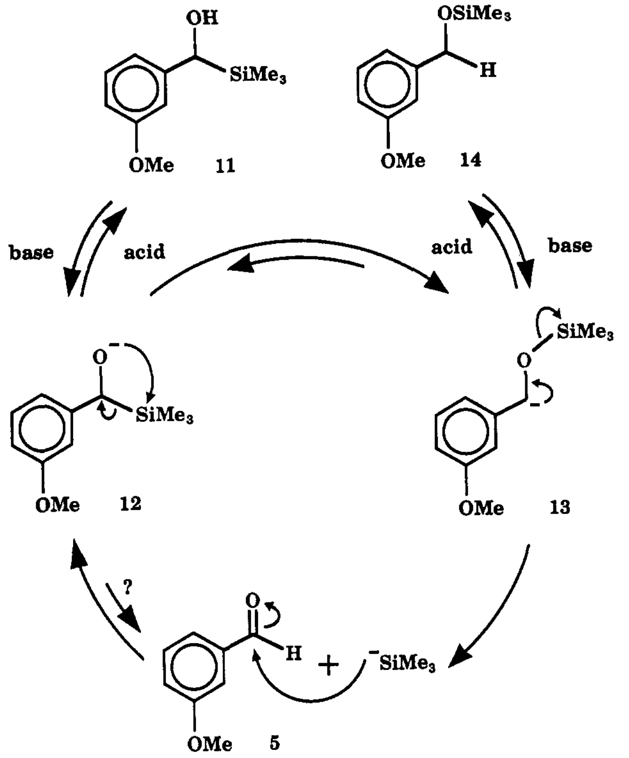


5. R = CHO
8. R = $CH(SCH_2CH_2CH_2S)$
9. R = $C(SiMe_3)(SCH_2CH_2CH_2S)$
10. R = $C(=O)SiMe_3$

ᵃ (a) Legend: $BF_3{\cdot}OEt_2$, $HS(CH_2)_3SH$, MeOH (98%); (b) (i) *n*-BuLi, −23 °C, (ii) Me_3SiCl (99%); (c) $HgCl_2$, $CaCO_3$, acetone, H_2O (90%); (d) $LiAlH_4$, 0 °C, THF (99%).

Preparation of α-Silyl Carbinol 11 and Silyl Ether 14. To provide evidence for the cycle shown in Scheme 1, we needed a pure α-(trimethylsilyl)carbinol, such as 11. Consequently, we prepared (3-methoxybenzoyl)trimethylsilane (10), the precursor of 11, from 3-methoxybenzaldehyde (5) by following Brook's procedure[4] (Scheme 3): Benzaldehyde 5 was treated with propane-1,3-dithiol in methanol to give 1,3-dithiane 8 (98% yield). Reaction of 8 with *n*-BuLi at −23 °C and then with Me_3SiCl produced 2-silyl-1,3-dithiane 9 in 99% yield. Upon hydrolysis in wet acetone with mercury(II) chloride and calcium carbonate, silyldithiane 9 was converted to benzoylsilane 10 (90% yield). Finally, we reduced 10 with $LiAlH_4$ in THF at 0 °C to afford pure α-(trimethylsilyl)carbinol 11 quantitatively. In addition, we prepared silyl ether 14 in 97% yield by silylating alcohol 4 with *N*,*O*-bis(trimethylsilyl)acetamide in anhydrous ethyl ether.[9]

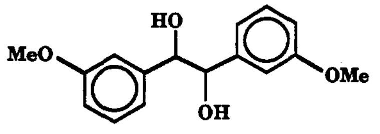
Scheme 4



Evidence for Existence of the Cycle Involving α-Silyl Alkoxides, α-Siloxy Carbanions, and Carbonyl Compounds Accompanied by $^-SiR_3$. If the cycle in Scheme 4 exists, alkoxide 12, carbanion 13, and benzaldehyde 5 (along with $^-SiMe_3$) should all three be generated as a mixture by initiation of any of the following three processes: O-deprotonation of alcohol 11, C-deprotonation of benzyl silyl ether 14, and 1,2-addition of benzaldehyde 5 with $^-SiMe_3$. To prove this point, we carried out a series of control experiments.

First, we treated alcohol 11 and benzyl silyl ether 14 individually with a base, including *n*-BuLi, KH, NaH, and *t*-BuLi, in the mixture of THF and HMPA. The reaction time was varied from 2 to 65 h, and the reactions were controlled from −78 °C to room temperature. The product compositions analyzed by GC are summarized in Table 1 (runs 1–8). In each of these reactions, we detected α-silyl alcohol 11, benzyl silyl ether 14 along with the corresponding benzyl alcohol 4, and benzaldehyde 5 in the reaction mixtures. Ready hydrolysis of trimethylsilyl ether 14 to alcohol 4 under the conditions employed was further confirmed by a control experiment.

Second, we treated $LiSiMe_3$ with aldehyde 5 in a mixture of THF and HMPA. The product composition is shown in Table 1 (run 9); in this reaction, diol 16 was isolated as the major product.



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Discussion

Oxidation Process. Hexamethyldisilane can act as an oxidant in organic reactions, such as in the conversion of hydrazines to 2-tetrazenes.[10] For oxidation of benzyl alcohol 4 to benzaldehyde 5 by use of $Me_3SiSiMe_3$ under basic conditions, a plausible mechanism is illustrated in

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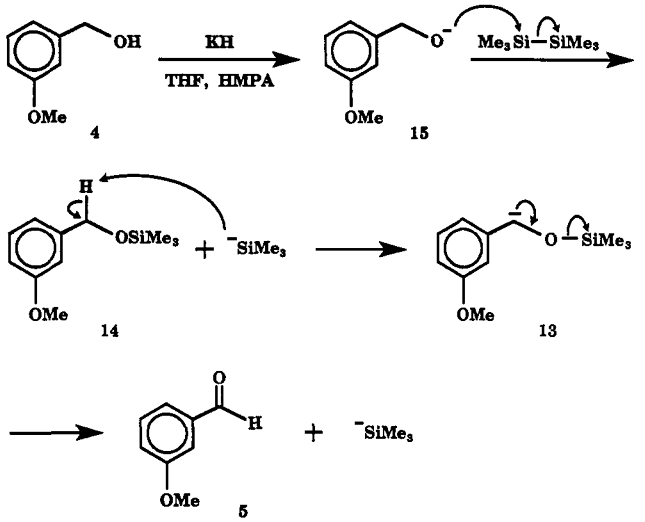
[9] Hwu, J. R.; Anderson, D. A.; Wang, N.; Buchner, M. M.; Gani, P.; Tsay, S.-C. *Chem. Ber.* 1990, *123*, 1667.

Table 1. Reaction Product Compositions (mol %) Determined by GC

	reaction conditions[a]				products (%)				
run no.	starting compound	base	temp (°C)[b]	time (h)	**4**	**5**	**11**	**14**	**16**
1	**11**	*n*-BuLi	−78	2	79.0	3.93	1.08	15.5	0.46
2	**11**	*n*-BuLi	−78 + 0	2 + 2	84.1	2.66	1.55	12.1	0.61
3	**11**	*n*-BuLi	−78 + 0 + rt	2 + 2 + 20	88.4	2.72	0.40	7.86	0.59
4	**11**	*n*-BuLi	rt	65	92.9	2.60	0.28	4.20	
5	**11**	KH	rt	40	81.3	14.7	0.22	3.76	
6	**11**	NaH	rt	48	95.8	0.38	0.07	3.76	
7	**14**	KH	rt	44	89.4	2.81	0.22	7.60	
8	**14**	*t*-BuLi	rt	48	96.9	2.26	<0.02	0.84	
9	**5**	$LiSiMe_3$	rt	48	21.3	9.55	0.65	3.42	65.1[c]

[a] A mixture of THF and HMPA was used as the solvent. [b] rt = room temperature. [c] The product was isolated in 45% yield.

Scheme 5



Scheme 5. First, the labile hydroxyl proton in **4** was removed by KH; the resultant alkoxide **15** then reacted with $Me_3SiSiMe_3$ to produce silyl ether **14** and $^-SiMe_3$. Abstraction of an acidic α-proton at the benzylic position in **14** with $^-SiMe_3$ gave the benzylic carbanion **13**,[1] which underwent a β-elimination to give benzaldehyde **5** along with $^-SiMe_3$. In the entire process, $Me_3SiSiMe_3$ can be regarded as a "counterattack reagent".[11]

By the same method used to convert silyl ether **14** to benzaldehyde **5**, we were able to oxidize silyl ether **6** to ketone **7** in 90% yield (Scheme 2). The driving force of these oxidations comes from the formation of a conjugated carbonyl functionality. In a previous communication,[8] we discussed the mechanism in detail for the conversion of **6** to **7**.

Interconversions among the Species in the Cycle. In Scheme 1, α-silylalkoxides **1** may undergo the Brook rearrangement[4] to give α-siloxy carbanions **2**. In contrast, Wright and West[12] found that the silyl-Wittig rearrangement may occur in α-siloxy carbanions, such as **2**, to give α-silylalkoxides **1**. These interconversions may involve an anionic pentacoordinate silicon intermediate with a three-membered ring. The equilibrium between **1** and **2**, however, depends upon their relative stabilities.[12]

Gilman and Lichtenwalter[1b,2] reported that 1,2-addition of $^-SiR_3$ to the carbonyl compound **3** gives the corresponding α-silylalkoxide (**1**; Scheme 1). A previous report describes the β-elimination of α-siloxy carbanions **2** to carbonyl compounds **3** and $^-SiR_3$.[8] In combination with these processes, we expect the coexistence of species **1**–**3** in a basic solution.

Our results (runs 1–9, Table 1) showed that the distributions among compounds **4**, **5**, **11**, and **14** were consistent in all reactions. Benzyl alcohol **4** was derived from hydrolysis of silyl ether **14**; thus, the total amount of **4** and **14** found in the reaction mixture represented the quantity of siloxy carbanion **13** in the cycle. Similarly, the presence of α-silyl alcohol **11** was a measure of the α-silylalkoxide **12** generated.

We found that the siloxy carbanion **13** was the major component among the three species in the equilibrium shown in Scheme 4, as reflected by the yields of 79–97% in total for **4** and **14** (Table 1, runs 1–8), whereas α-silylalkoxide **12** was the minor component (<1.1% yields for **11**). The benzaldehyde **5**, which has a higher oxidation state than alcohol **11** and silyl ether **14**, was detected in 0.38 to 14.7% yields. In addition, a longer reaction time disfavored the formation of α-silylalkoxide **12** (cf. the yields of **11** in runs 3 and 4 of Table 1).

Reaction Byproduct and the Possibility of Alternative Mechanisms. Diol **16** was isolated as the major product when we treated aldehyde **5** with $LiSiMe_3$ (Table 1, run 9). It was probably generated by electron transfer[13,14] from the $^-SiMe_3$ anion to aldehyde **5**, followed by coupling of the resultant two $m\text{-}MeOC_6H_4CH(O^-)^\bullet$ radical anions, or from the reaction of **13** with aldehyde **5**.

Direct reversion of aldehyde **5** to siloxy carbanion **13** requires addition of the $^-SiMe_3$ species to the carbonyl oxygen of **5** (Scheme 4). To the best of our knowledge, such an "abnormal" 1,2-addition was first proposed by Gilman et al. in 1953; it involves the $^-SiPh_3$ species and benzophenone.[1a,2,15] Nevertheless, he concluded later that the silyl ether products were obtained through a two-step process: a "normal" 1,2-addition followed by the Brook rearrangement[1b,4] (cf. the processes **3** → **1** → **2** in Scheme 1). On the other hand, we did not obtain any evidence to indicate the feasibility for the reversion **12** → **5**. The possibility of its existence, however, cannot be excluded completely, given the microscopic viewpoint.

Different mechanisms were considered to account for the interconversions shown in Schemes 1 and 4. Analogous to the mechanism for the Cannizzaro reaction[16] was the hydride transfer from alkoxide **12** to aldehyde **5**, giving benzyl alcohol **4**; then the benzoylsilane **10** would have to

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(10) Hwu, J. R.; Wang, N.; Yung, R. T. *J. Org. Chem.* **1989**, *54*, 1070.

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(15) Gilman, H.; Wittenberg, D. *J. Org. Chem.* **1958**, *23*, 501.

be generated as the byproduct. The absence of compound **10** in the reaction mixtures shown in Table 1 allows us to exclude this mechanism. Similarly, the hydride transfer mechanism involved in the Tishchenko reaction[17] cannot be applied to our reactions because we did not detect any ester (i.e., *m*-$MeOC_6H_4COOCH_2C_6H_4$-*m*-OMe) resulting from the dimerization of 3-methoxybenzaldehyde (**5**).

Reaction of an alkoxide with hexamethyldisilane gives the corresponding silyl ether and $^-SiMe_3$.[18] In contrast, decomposition of alkoxides by a hydride transfer, such as those in the Oppenauer reaction,[19] requires a special catalyst (e.g., aluminum alkoxides) and an efficient acceptor (e.g., carbonyl compounds). Lack of both factors in the conversion of alcohol **4** to aldehyde **5** allows us to minimize, but not disregard, the possibility of a hydride transfer from alkoxide **15** to $Me_3SiSiMe_3$ giving aldehyde **5** and $HSiMe_3$.

Conclusion

Conversion of 3-methoxybenzyl alcohol (**4**) to 3-methoxybenzaldehyde (**5**) was carried out by use of $Me_3SiSiMe_3$ under basic conditions. Reaction of benzyl silyl ether **6** with $LiSiMe_3$ gave the corresponding ketone (**7**) as the major product. These oxidation processes likely involved a step of β-elimination of α-siloxy carbanions. Results from a series of experiments showed that the interconversions constituted a cycle among α-silylalkoxides, α-siloxy carbanions, and carbonyl compounds accompanied by $^-SiR_3$. This newly proposed cycle involves the Brook rearrangement, the silyl-Wittig rearrangement, a β-elimination, and a 1,2-addition.

Experimental Section

General Considerations. Gas chromatography analyses were performed on a Hewlett-Packard 5794A instrument equipped with a 12.5-m cross-linked methylsilicone gum capillary column (0.2 mm i.d.). The conditions were as follows except as stated otherwise: injector temperature 260 °C; column temperature program initial temperature 110 °C (duration 7.00 min), increment rate 15 °C/min; final temperature 250 °C. Purification by gravity column chromatography was carried out by use of EM Reagents silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial thin-layer chromatography were performed on a Model 7924T Chromatotron from Harrison Research. The plates were coated with EM Reagents silica gel 60 PF_{254} containing gypsum.

3-Methoxybenzaldehyde (5). Potassium hydride (35% in mineral oil, 138 mg, 1.21 mmol) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum and was washed with hexanes (3 × 3 mL). Hexanes were removed to give KH as a white powder. Tetrahydrofuran (16 mL) and alcohol **4** (167 mg, 1.21 mmol) were added, and the resultant suspension was stirred at room temperature for 2 h. The solution of $Me_3SiSiMe_3$ (212 mg, 1.45 mmol) in HMPA (4.0 mL) was then added, and the reaction mixture was stirred at room temperature for an additional 55 h. The mixture was then worked up by addition of water (15 mL), followed by extraction of the aqueous layer with ethyl ether (3 × 15 mL). The organic phase was then washed with water (3 × 10 mL) and brine solution (2 × 10 mL), dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure to afford a pale yellow oil. The crude product was purified with a Chromatotron (1-mm plate; 20% EtOAc in hexanes as eluant) to give **5** (31.0 mg, 0.25 mmol) in 20% yield: TLC R_f 0.43 (20% EtOAc in hexanes); GC t_R 2.11 min (it was the exclusive peak in the chromatogram); ^1H NMR ($CDCl_3$) δ 3.85 (s, 3 H, OCH_3), 7.15–7.71 (m, 4 H, C_6H_4), 9.96 (s, 1 H, CHO); IR (neat) 3064 (w), 3006 (w), 2953 (w), 2834 (m), 2731 (w), 1697 (s), 1593 (s), 1486 (s), 1462 (s), 1390 (m), 1322 (m), 1268 (s), 1148 (s), 1041 (s), 929 (m), 785 (m), 738 (m), 682 (m) cm^{-1}; MS *m/e* (relative intensity) 136 (M^+, 100), 135 (96), 119 (1), 107 (31), 92 (18), 77 (30), 65 (18), 51 (8). Its spectral data are identical with those of an authentic sample of 3-methoxybenzaldehyde (**5**).[20]

Cyclopropyl Phenyl Ketone (7). (Trimethylsilyl)lithium was prepared by reaction of $Me_3SiSiMe_3$ (38.6 mg, 0.263 mmol) with MeLi (1.4 M in hexanes, 0.184 mL, 0.258 mmol) in HMPA (0.184 mL) at −78 °C.[21] While the reaction mixture was kept at 0 °C, benzyl silyl ether **6** (37.8 mg, 0.171 mmol) was added and the resultant dark red solution was stirred at room temperature for 24 h. The reaction was worked up as described above to give a pale yellow oil. After purification by use of a Chromatotron, phenone **7** (22.5 mg, 0.154 mmol) was obtained as a yellow oil in 90% yield: TLC R_f 0.32 (10% EtOAc in hexanes); GC (column temperature 120 °C) t_R 3.09 min; ^1H NMR ($CDCl_3$) δ 0.80–1.32 (m, 4 H, 2 × CH_2), 2.40–2.85 (m, 1 H, COCH), 7.22–8.15 (m, 5 H, C_6H_5); IR (neat) 3190 (m), 1665 (s), 1580 (m), 1455 (s), 1400 (s), 1260 (s), 1200 (w), 1035 (w), 1025 (m), 990 (s), 840 (br), 820 (br), 780 (br), 700 (br, s), 630 (s) cm^{-1}. Its spectral data are identical with those of an authentic sample of cyclopropyl phenyl ketone.[20]

2-(3-Methoxyphenyl)-1,3-dithiane (8). To a solution of **5** (2.00 g, 14.7 mmol) in methanol (40 mL) was added 1,3-propanedithiol (1.45 g, 13.4 mmol). To the mixture was then added boron trifluoride etherate (2.08 g, 14.7 mmol), which had been cooled to 0 °C. The reaction solution was stirred at room temperature for 40 h. After removal of solvents, the residual oil was dissolved in diethyl ether (200 mL) and this solution washed with 10% NaOH (3 × 25 mL), water (50 mL), saturated NH_4Cl (50 mL), and brine solution (50 mL). Then it was dried over $MgSO_4$(s) and filtered. Evaporation of the filtrate under reduced pressure and then recrystallization of the residue with hexanes afforded 1,3-dithiane **8** (2.97 g, 13.1 mmol) as a white solid in 98% yield: mp 59.5–61.5 °C; TLC R_f 0.43 (20% EtOAc in hexanes); GC (column temperature program initial temperature 130 °C (duration 2.00 min), increment rate 10 °C/min, final temperature 250 °C) t_R 9.41 min; ^1H NMR ($CDCl_3$) δ 1.71–2.35 (m, 2 H, $SCCH_2CS$), 2.62–3.13 (m, 4 H, 2 × CH_2S), 3.80 (s, 3 H, OCH_3), 5.13 (s, 1 H, SCHS), 6.67–7.38 (m, 4 H, C_6H_4); IR (neat) 3040 (w, sh), 2995 (m), 2925 (s), 2885 (s), 2825 (s), 1590 (s), 1485 (s), 1420 (s), 1315 (s), 1270 (s), 1145 (s), 1045 (s), 910 (m), 870 (m), 760 (s), 695 (s) cm^{-1}; exact mass calcd for $C_{11}H_{14}OS_2$ 226.0486, found (70 eV) 226.0488. Anal. Calcd: C, 58.39; H, 6.24; S, 28.29. Found: C, 58.28; H, 6.30; S, 28.37.

2-(3-Methoxyphenyl)-2-(trimethylsilyl)-1,3-dithiane (9). In a 50-mL one-necked, round-bottomed flask, **8** (2.00 g, 8.85 mmol) was dissolved in THF (20 mL). The solution was cooled to −23 °C, and *n*-BuLi (2.5 M in hexanes, 4.25 mL, 10.6 mmol) was then added. After the mixture was stirred for 40 min, chlorotrimethylsilane (1.15 g, 10.6 mmol) was added and stirring was continued at room temperature for 16 h. The reaction was then quenched with water (10 mL), and the mixture was extracted with diethyl ether (3 × 15 mL). The organic layers were combined, washed with saturated $NaHCO_3$ solution (15 mL), water (15 mL), and brine solution (15 mL), and then dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The crude product was chromatographed through silica gel with hexanes as eluant to give **9** (2.63 g, 8.82 mmol) as a pale yellow oil in 99% yield:

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(20) Compounds are available from Aldrich Chemical Co.

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TCL R_f 0.54 (10% EtOAc in hexanes); GC (column temperature program initial temperature 110 °C (duration 4.00 min), increment rate 15 °C/min, final temperature 250 °C) t_R 12.07 min; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H, $Si(CH_3)_3$), 1.71–2.15 (m, 2 H, $SCCH_2$-CS), 2.23–3.01 (m, 4 H, 2 × CH_2S), 3.82 (s, 3 H, OCH_3), 6.58–7.55 (m, 4 H, C_6H_4); IR (neat) 3060 (w), 2945 (s), 2900 (s), 2825 (m), 1590 (s), 1475 (s, br), 1420 (s), 1310 (m), 1285 (s), 1250 (s), 1125 (m), 1050 (s), 1010 (m), 930 (m), 920 (m), 840 (s, br), 745 (m), 700 (s) cm^{-1}; exact mass calcd for $C_{14}H_{22}OS_2Si$ 298.0881, found (70 eV) 298.0885. Anal. Calcd: C, 56.36; H, 7.44; Si, 9.39; S, 21.45. Found: C, 56.25; H, 7.52; Si, 9.28; S, 21.51.

(3-Methoxybenzoyl)trimethylsilane (10). To a solution of 1,3-dithiane **9** (2.73 g, 9.15 mmol) in a mixture of acetone and toluene (3:1, 120 mL) were added $HgCl_2$ (37.3 g, 0.137 mmol), $CaCO_3$ (4.58 g, 45.8 mmol), and water (1.81 mL, 0.10 mmol). The reaction mixture was heated at reflux for 20 h and then filtered and evaporated under reduced pressure to give a yellow liquid with some white solid. The crude product was dissolved in a mixture of water (30 mL) and diethyl ether (30 mL). After separation, the aqueous layer was extracted with diethyl ether (3 × 20 mL). The organic layers were combined, washed with brine solution, and then dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. Purification of the residue by chromatography (10% EtOAc in hexanes as eluant) provided **10** (1.72 g, 8.27 mmol) as a yellow liquid in 90% yield: TLC R_f 0.51 (10% EtOAc in hexanes); GC (column temperature program initial temperature 110 °C (duration 4.00 min), increment rate 15 °C/min, final temperature 250 °C) t_R 6.91 min; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9 H, $Si(CH_3)_3$), 3.84 (s, 3 H, OCH_3), 6.96–7.61 (m, 4 H, C_6H_4); IR (neat) 3065 (w, br), 3005 (w), 2960 (m), 2910 (w), 2840 (w), 1615 (m), 1580 (s), 1485 (m, br), 1425 (m), 1255 (s), 1170 (w, sh), 1155 (m), 1045 (m), 850 (s), 795 (s), 760 (w) cm^{-1}; exact mass calcd for $C_{11}H_{16}O_2Si$ 208.0920, found (70 eV) 208.0921. Anal. Calcd: C, 63.43; H, 7.75; Si, 13.44. Found: C, 63.28; H, 7.79; Si, 13.51.

3-Methoxy-α-(trimethylsilyl)benzyl Alcohol (11).[22] To a solution of the benzoylsilane **10** (150 mg, 0.721 mmol) in THF (14 mL) was added $LiAlH_4$ (1.0 M in diethyl ether, 380 μL, 0.38 mmol) at 0 °C. The yellow mixture turned clear and colorless immediately. The reaction was monitored by TLC, and no starting ketone was detected after 20 min at 0 °C. The reaction was quenched by addition of aqueous NaOH solution (10%, 0.2 mL) to give turbid precipitations. The mixture was then filtered through Celite, and the filtrate was washed with saturated NH_4-Cl solution (2 × 5 mL) water (5 mL), and brine solution (5 mL), and then dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. Purification of the residue by a Chromatotron (1-mm plate; 5% EtOAc in hexanes as eluant) afforded **11** (151 mg, 0.718 mmol) as a colorless oil in 99% yield: TCL R_f 0.25 (10% EtOAc in hexanes); GC t_R 9.30 min (it was the exclusive peak in the chromatogram); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9 H, $Si(CH_3)_3$), 1.65 (br, s, 1 H, OH), 3.79 (s, 3 H, OCH_3), 4.49 (s, 1 H, $OCHSiMe_3$), 6.58–7.29 (m, 4 H, C_6H_4); IR (neat) 3410 (w, br), 2970 (m), 2850 (w), 1595 (m, br), 1475 (m, br), 1255 (s), 1150 (m), 1050 (m, br), 1010 (m, br), 845 (s), 775 (m), 710 (s) cm^{-1}; exact mass calcd for $C_{11}H_{18}O_2Si$ 210.1076, found (70 eV) 210.1076. Anal. Calcd: C, 62.82; H, 8.63; Si, 13.32. Found: C, 62.91; H, 8.75; Si, 13.42.

3-Methoxybenzyl Trimethylsilyl Ether (14). To a solution of alcohol **4** (327 mg, 2.37 mmol) in diethyl ether (12 mL) was added *N,O*-bis(trimethylsilyl)acetamide (481 mg, 2.37 mmol). The resultant clear mixture was stirred at room temperature for 40 h. After the solvent was evaporated, the residue was purified with a Chromatotron (2-mm plate; 5% EtOAc in hexanes as eluant) to afford **14** (480 mg, 2.29 mmol) in 97% yield: TLC R_f 0.57 (10% EtOAc in hexanes), 0.73 (20% EtOAc in hexanes); GC t_R 6.11 min (it was the exclusive peak in the chromatogram); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 3.80 (s, 3 H, OCH_3), 4.67 (s, 2 H, $SiOCH_2Ph$), 6.62–7.31 (m, 4 H, C_6H_4); IR (neat) 3040 (w, br), 3010 (w), 2960 (s), 2900 (m), 2845 (m), 1595 (m, br), 1460 (m, br), 1260 (s), 1155 (m), 1075 (m), 1055 (m), 875 (s), 845 (s), 765 (w, br), 695 (m) cm^{-1}; exact mass calcd for $C_{11}H_{18}O_2Si$ 210.1076, found (70 eV) 210.1078. Anal. Calcd: C, 62.82; H, 8.63; Si, 13.32. Found: C, 62.71; H, 8.65; Si, 13.24. Addition of aqueous HCl solution (1.0 M, 1.0 mL) to a flask containing silyl ether **14** (102 mg) in THF (5.0 mL) afforded a mixture of alcohol **4** and intact **14** in a ratio between 5.2:1 and 320:1 in 3–180 min. The products were analyzed by TLC and GC; purification of the products was carried out by use of the Chromatotron as described above.

Reaction of 3-Methoxy-α-(trimethylsilyl)benzyl Alcohol (11) with Bases. With *n*-BuLi. A solution containing alcohol **11** (100.1 mg, 0.476 mmol) and a mixture of THF and HMPA (4:1, 10 mL) was cooled at −78 °C. To this solution was added *n*-BuLi (2.5 M in hexanes, 210 μL, 0.523 mmol), and this mixture was stirred at −78 °C for 2 h. While the reaction mixture was warmed to 0 °C, a portion of the solution (~3 mL) was withdrawn and neutralized with aqueous HCl solution (1.0 M, 0.5 mL). After the mixture was diluted with water (2 mL), the aqueous layer was separated and extracted with diethyl ether (3 × 3 mL). The organic layers were combined, washed with water (4 × 3 mL) and brine solution (2 × 3 mL), and then dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. This oily residual was labeled as product A1. After the original reaction mixture was stirred at 0 °C for 2 h, another portion (~3 mL) was withdrawn and worked up as described above. The second product was labeled as A2. The reaction was quenched with aqueous HCl solution (0.5 mL) followed by addition of water (3 mL) after an additional 20 h at room temperature, and the mixture was worked up as described above. The third product was labeled as A3. The compositions (mol %) of these three crops were analyzed by GC. A1: **4** t_R 3.22 min, 79.0%; **5**, t_R 2.11 min, 3.93%; **11**, t_R 9.32 min, 1.08%; **14**, t_R 6.11 min, 15.5%; **16**, t_R 15.91 min, 0.46%. A2: **4**, 84.1%; **5**, 2.66%; **11**, 1.55%; **14**, 12.1%; **16**, 0.61%. A3: **4**, 88.4%; **5**, 2.72%; **11**, 0.40%; **14**, 7.86%; **16**, 0.59%. Another run was carried out at room temperature for 65 h showed the composition **4**:**5**:**11**:**14** = 92.9:2.60:0.28:4.20.

With KH. Potassium hydride (35% in mineral oil, 72.0 mg, 0.628 mmol) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum, and was washed with hexanes (3 × 3 mL). Hexanes were removed to give KH as a white powder. To this powder was added alcohol **11** (120.0 mg, 0.571 mmol) and a mixture of THF and HMPA (4:1, 15 mL). After 40 h, the reaction mixture was worked up as described above to give a pale yellow oil (98 mg). Its composition (mol %) was analyzed by GC: **4** t_R 3.25 min, 81.3%; **5**, t_R 2.09 min, 14.7%; **11**, t_R 0.31 min, 0.22%; **14**, t_R 6.03 min, 3.76%.

With NaH. The procedure of the reaction with KH described above was followed. The reagents added were NaH (59.5% in mineral oil, 21.1 mg, 0.523 mmol), a mixture of THF and HMPA (4:1, 15 mL), and alcohol **11** (109 mg, 0.476 mmol). After 48 h, an oily product was obtained (98.0 mg) and its composition (mol %) was analyzed by GC: **4**, t_R 3.21 min, 95.8%; **5**, t_R 2.06 min, 0.38%; **11**, t_R 9.31 min, 0.07%; **14**, t_R 5.95 min, 3.76%.

Reaction of 3-Methoxybenzyl Trimethylsilyl Ether (14) with Bases. With KH. The procedure of the reaction of **11** with KH was followed. The reagents added were KH (35% in mineral oil, 72.1 mg, 0.628 mmol), a mixture of THF and HMPA (4:1, 15 mL), and silyl ether **14** (121 mg, 0.571 mmol). After 44 h, the reaction mixture was worked up as described above to give an oily product. Its composition (mol %) was analyzed by GC: **4**, t_R 3.40 min, 89.4%; **5**, t_R 2.09 min, 2.81%; **11**, t_R 9.31 min, 0.22%; **14**, t_R 6.11 min, 7.60%.

With *t*-BuLi. To a solution of the silyl ether **14** (130.0 mg, 0.618 mmol) in a mixture of THF and HMPA (4:1, 15 mL) was added *t*-BuLi (1.7 M in pentane, 0.43 mL, 0.74 mmol) at −78 °C. The resultant brownish red mixture was stirred at room temperature for 48 h. The reaction mixture was worked up as described above to give a pale yellow oil (110 mg). The composition (mol %) of the product was analyzed by GC: **4**, t_R 3.24 min, 96.9%; **5**, t_R 2.07 min, 2.26 %; **11**, trace (<0.02%); **14**, t_R 6.02 min, 0.84%.

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[22] Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431.

Reaction of 3-Methoxybenzaldehyde (5) with $LiSiMe_3$. (Trimethylsilyl)lithium was prepared by reaction of $Me_3SiSiMe_3$ (357 mg, 2.44 mmol) with MeLi (1.4 M in hexanes 1.39 mL, 1.95 mmol) in a mixture of THF and HMPA (4:1, 20 mL) at −78 °C.[21] While the reaction mixture was kept at 0 °C, aldehyde **5** (222 mg, 1.63 mmol) was added and the resultant dark red solution was stirred at room temperature for 48 h. The reaction mixture was worked up as described above to give a pale yellow oil (273 mg). The composition (mol %) of the crude product was determined by GC: **4**, t_R 3.22 min, 21.3%; **5**, t_R 2.12 min, 9.55%; **11**, t_R 9.11 min, 0.65%; **14**, t_R 6.09 min, 3.42%; **16**, t_R 15.97 min, 65.1%. Purification of the crude product with a Chromatotron (1-mm plate, solvent program 40% EtOAc in hexanes as eluant) afforded **16** as a colorless oil in 45% yield (101 mg, 0.370 mmol): GC t_R 15.91 min; ^1H NMR ($CDCl_3$) δ 2.19 (br, s, 2 H, 2 × OH), 3.74 (s, 6 H, 2 × OCH_3), 4.78 (s, 2 H, 2 × OCHPh), 6.73–7.36 (m, 8 H, 2 × C_6H_4); IR (neat) 3400 (m, br), 2940 (w), 2840 (w), 1595 (s), 1490 (s), 1455 (s, br), 1320 (m), 1260 (s), 1160 (m), 1040 (s), 880 (w), 775 (m), 720 (m), 710 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 662. Found: C, 70.13; H, 6.71.

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