thout subsequent polymerization [K. Narasaka, E. Balk, and T. Mukaiyama, *Chem. Lett.*, 1041 (1975)]. The factors controlling reactivity of a substrate in any given reaction mode are unknown and at present the behavior of a given substrate under a particular set of reaction conditions cannot be predicted.

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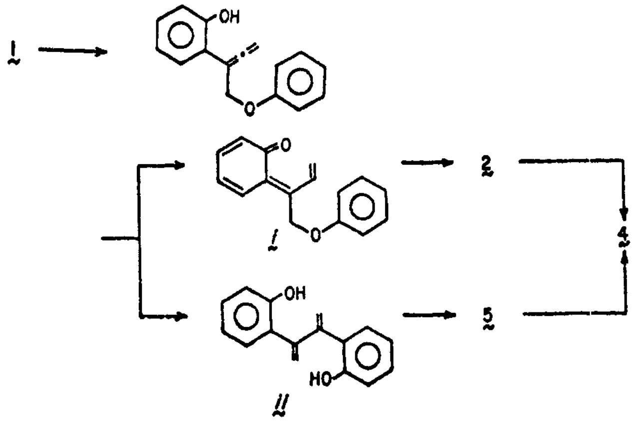
(20) An alternative mechanism involving direct formation of **5** from **1** by a "double" Claisen rearrangement followed by ionic rearrangement as shown below may be excluded from consideration. If this mechanism was operating one might expect to isolate **5** from reaction of **1** with heavy metal ions. Additionally, the absence of **5** in all crude $AlCl_3$ catalyzed reaction mixtures, even when the reaction was interrupted at low conversion, makes this path seem unlikely. It would appear that the 1,5-hydrogen shift leading to i is faster than the 3,3 process leading to ii. Schmid (ref 2) has indicated that the initial thermal rearrangement is slower than the 1,5-hydrogen shift in the rearrangement of phenyl propynyl ethers into 2*H*-chromenes.



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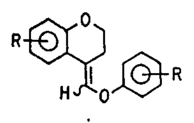
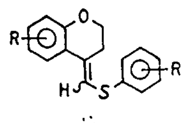
(22) A. A. Schegoler, W. A. Smit, S. A. Khurshudyan, V. A. Chertkov, and V. F. Kucherov, *Synthesis*, 324 (1977); H. Martens, F. Janssens, and G. Hoornaert, *Tetrahedron*, **31**, 177 (1975); A. A. Schegoler, W. A. Smit, V. F. Kucherov, and R. Caple, *J. Am. Chem. Soc.*, **97**, 6604 (1975); H. Martens and G. Hoornaert, *Synth. Commun.*, **2**, 147 (1972).

(23) As pointed out by a referee, the spirocyclic intermediate produced by the Friedel–Crafts process could be formed reversibly. On this basis it was suggested that the observed mode of fusion might ultimately prevail. However, under equilibrating conditions, formation of charge at the benzylic position would most probably result in formation of the vinyl ether, i, or products derived from it (rather than from **2**). Support for this contention derives from the well-known thermodynamic stability of vinyl ethers over allyl ethers. Additionally, treatment of the related sulfur system ii with trifluoroacetic acid in refluxing chloroform produces the corresponding vinyl sulfide in excellent yield (ref 23b) presumably via a benzylic cation. We therefore do not consider formation of **2** by a Friedel–Crafts type alkylation likely. (b) B. S. Thyagarajan, K. C. Majumdar, and D. K. Bates, *J. Heterocycl. Chem.*, **12**, 59 (1975).



i



ii

(24) Reactions at the triple bond of aryl 2-propynyl ethers have also been sought but not found. Thus, phenyl 2-propynyl ether reacts with $PhCO^+$ $AlCl_4^-$ producing 4-benzoylphenyl 2-propynyl ether in good yield. When the 4 position of the ether is blocked, ether cleavage producing the aryl benzoate occurs: unpublished observations of M. Dziobak, 1978.

.(25) This paper is dedicated to the memory of Professor H. Schmid.

Reactions of Ketones with Sodium Hydride or Potassium Hydride in the Presence of Trimethylsilyl Chloride. Preparation of Trimethylsilyl Enol Ethers[1]

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Reactions of cyclohexanone with NaH and Me_3SiCl in various solvents yielded predominantly (90–97%) the silyl enol ether **2** resulting from enolization, with only a few percent of the alkyl silyl ether **1** resulting from initial reduction. Similar reactions with KH and Me_3SiCl proceeded well only in dioxane to give >99% of **2**. Cyclohexanone, 2-methylcyclohexanone, acetophenone, and 2-heptanone were converted to trimethylsilyl enol ethers in good yields by this method.

Alkali metal hydrides are widely used as bases in organic synthesis and have been especially useful for the conversion of carbonyl compounds to metal enolates.[3–5] Sodium hydride has been most commonly used.[3] Potassium hydride has recently been shown to be much more reactive than sodium hydride and is an excellent reagent for the generation of potassium enolates.[4] Lithium hydride, although comparatively unreactive, has been used in a few cases to generate lithium enolates.[5]

Some hydrides of other metals, particularly complex metal hydrides such as $NaBH_4$ and $LiAlH_4$, are widely used as reducing agents in organic synthesis;[6] these hydrides will usually reduce a carbonyl group rather than abstract an enolizable hydrogen. In contrast, alkali metal hydrides have been reported to reduce organic compounds relatively infrequently.[7–10] Reductions of carbonyl groups have been reported only in special cases; for example, sodium hydride has been shown to reduce carbonyl compounds which have no enolizable hydrogens or which are not readily enolized.[7]

The reactions of alkali metal hydrides with carbonyl compounds to give metal enolates are commonly believed to be catalyzed by alkoxides (formed from traces of alcohol impurities in the reaction mixtures) as the proton-transfer agents,[3c,i] since the hydrides are insoluble in common organic solvents.[4c,11] Thus, catalytic amounts of ethanol have been used to initiate sluggish reactions of metal hydrides.[3c,4e] We were intrigued by the possibility that the reactions of ketones with alkali metal hydrides might proceed by initial *reduction* of a small fraction of the ketone to the corresponding alkoxide, which would then catalyze enolate formation by acting as the proton-transfer agent (Scheme I). We have therefore studied the reactions of several ketones with sodium, potassium, and lithium hydrides in the presence of trimethylsilyl chloride, a reagent expected to trap enolate anions or alkoxide anions as they are formed.[12,13] To the extent that reduction takes place, an alkyl trimethylsilyl ether (e.g., **1**) should be formed; to the extent that direct enolization takes place, an alkenyl trimethylsilyl ether (trimethylsilyl enol ether, e.g., **2**) should be

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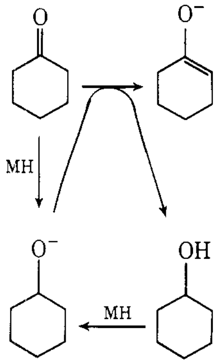
Table I. Reactions of Cyclohexanone with MH/Me_3SiCl

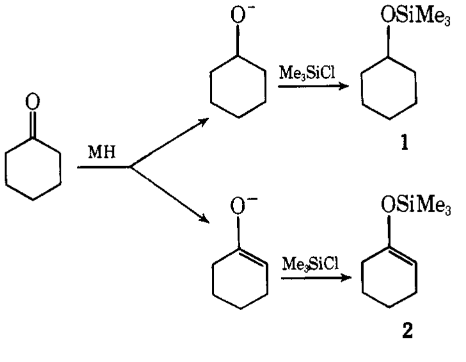
		% yields[a] of 1 and 2 at various reaction times					
		2 h		12 h		24 h	
MH	solvent[b]	1	2	1	2	1	2
LiH	dioxane	0.1	0.1	5.6	4.1	16	11
LiH	THF	0.04	0.04	2.3	2.8	3.6	3.0
NaH	hexane	0.2	30	4.0	73	4.9	95
NaH	heptane	2.6	108[c]				
NaH	toluene (75–80 °C)	1.3	40	2.7	95		
NaH	toluene	2.3	112[d]				
NaH	dioxane (75–80 °C)	1.4	39	4.7	78	5.0	96[e]
NaH[f]	dioxane	4.6	70	6.3	98		
NaH[f]	dioxane	3.1	68	7.1	104		
NaH[g]	dioxane	3.7	83	5.4	99		
NaH[g]	dioxane	5.3	93	5.5	92		
NaH[g,h]	dioxane	5.2	94	5.8	94		
NaH[i]	dioxane	3.4	100	4.5	105		
NaH	THF	0.1	0.1	0.1	0.3	0.3	16
NaH	DME[j] (75–80 °C)	1.2	9.4	5.9	23		
NaH	DME	0.0	3.3	3.9	44	9.5	63
NaH	DME[j]-HMPA (4:1)	0.1	0.1	7.4	33	16	49
KH	heptane[k]	0.0	3.7	0.0	3.6	0.1	3.4
KH	toluene[l]	0.0	4.9	0.0	4.1	0.1	2.4
KH	dioxane	0.3	106	0.5	99		
KH	dioxane (crown)[m]	0.0	0.1	0.3	84		
KH	THF	0.0	0.9	0.0	2.3	0.0	5.0
KH	THF[j] (crown)[m]	0.0	0.0	0.0	0.0	0.0	0.0[n]

[a] Yields were determined by VPC (SE-30 column)[23] using *n*-undecane as an internal standard (relative detector response calibrated). [b] At reflux temperature unless otherwise indicated. See Experimental Section for purification of solvents and general procedure. [c] A sample taken after 1 h was similar. [d] Sample taken at 1 h. [e] Sample taken at 18 h. [f] Supplied by Alfa Inorganics, 57% dispersion in mineral oil. [g] Supplied by Alfa Inorganics, 50% dispersion in mineral oil. [h] The NaH was washed with three portions of a solution of naphthalene in THF (distilled from sodium/benzophenone) to remove traces of sodium metal; a similar reaction in which the NaH was washed with three portions of a solution of naphthalene in DME gave similar results. [i] Supplied by Research Organic/Inorganic Chemical Corp., Belleville, N.J., 50% dispersion in mineral oil. [j] Distilled from sodium and lithium aluminum hydride. [k] Distilled from calcium hydride. [l] Distilled (under reduced pressure) from lithium aluminum hydride. [m] 18-Crown-6 (0.01 equiv) added to reaction mixture. [n] A sample taken after 48 h showed no formation of 1 or 2; gas evolution on workup indicated that KH was still present.

Scheme I



formed. In the course of this investigation, we have found conditions under which trimethylsilyl enol ethers can be prepared from ketones in good yields.



Results and Discussion

Reactions of cyclohexanone with alkali metal hydrides in the presence of trimethylsilyl chloride in a variety of solvents are summarized in Table I. Under all conditions in which a significant degree of reaction took place, the product (**2**) expected from the enolization pathway overwhelmingly predominated over the product (**1**) expected from the reduction pathway.[14] With potassium hydride in dioxane, the trimethylsilyl enol ether **2** was almost the exclusive product.

The rates of the reactions are seen to be strongly dependent on the solvent used; in no case was a significant conversion to trimethylsilyl ethers observed in the more polar (or better coordinating) solvents THF, DME, or DME–HMPA. In line with these observations, the addition of 18-crown-6 to some of the (KH) reaction mixtures caused a decrease in the initial reaction rate.[15] Reactions with lithium hydride were very sluggish in all solvents studied. Reactions with sodium hydride resulted in good yields of trimethylsilyl ethers in a number of solvents. Reactions with potassium hydride were surprisingly sluggish in all solvents studied except dioxane, in which reaction was fairly rapid.

The reactions of an unsymmetrical ketone, 2-methylcyclohexanone, with sodium hydride and with potassium hydride in the presence of trimethylsilyl chloride were investigated, and the results are shown in Table II. As with cyclohexanone, the major products were trimethylsilyl enol ethers (**4a,b**). Under all conditions, both double bond isomers were formed, that having the more substituted double bond (**4b**) being slightly favored in heptane and toluene, and that having the less-substituted double bond (**4a**) being favored in dioxane.

Since trimethylsilyl enol ethers were formed in good yields

Table II. Reactions of 2-Methylcyclohexanone with MH/Me_3SiCl[a]

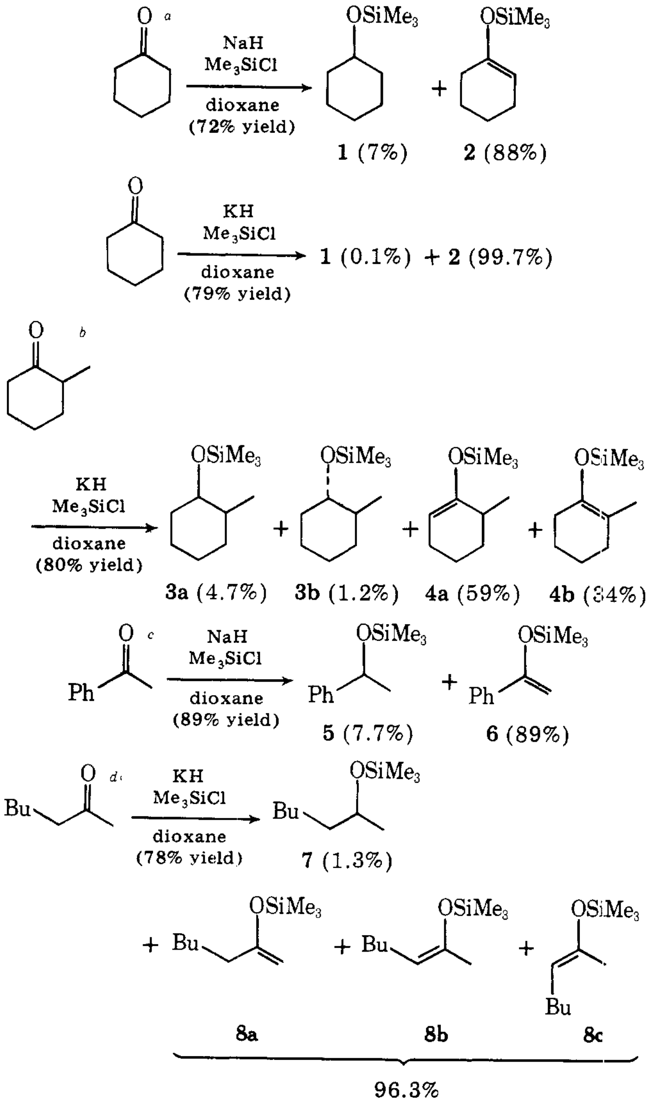
MH	solvent (reflux)	time, h	% product ratios[b] ketone	3a	3b	4a	4b
NaH	heptane	8	3	5	2	25	65
NaH	toluene	6	0	5	3	21	71
NaH	dioxane	12	5	10	3	47	35
KH	dioxane	2	9	3	<1	63	24

[a] See Experimental Section for general procedure. [b] Area ratios determined by VPC (SF-96 column).[23]

under some of the reaction conditions,[16] several ketones were treated with metal hydrides in the presence of trimethylsilyl chloride on a preparative scale to demonstrate the synthetic value of these reactions. The results are shown in Scheme II. The yields represent isolated yields of distilled material. The most favorable conditions for the synthesis of trimethylsilyl enol ethers were found to be KH with Me_3SiCl in dioxane; with NaH the products were usually contaminated with small amounts of reduction product.

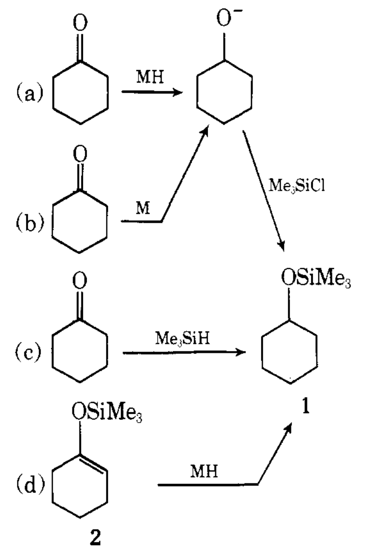
Although *reduction* of the carbonyl group by the alkali metal hydrides (in the presence of trimethylsilyl chloride) is clearly not a major reaction under any of the conditions studied, the products expected from reduction (alkyl trimethylsilyl ethers) were present in measurable amounts under most reaction conditions. In principle, the formation of these products could be accounted for by several pathways (see Scheme III) other than that involving direct reduction of the carbonyl group by the metal hydride (path a).

Scheme II



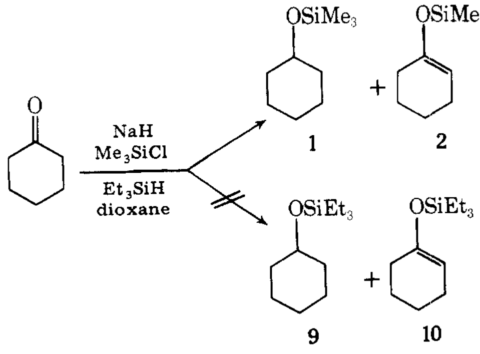
[a] Registry no.: 108-94-1. [b] Registry no.: 583-60-8. [c] Registry no.: 98-86-2. [d] Registry no.: 110-43-0.

Scheme III



One possible pathway for the formation of alkyl trimethylsilyl ethers involves reduction of the carbonyl group by an alkali metal impurity (path b). Some commercial samples of alkali metal hydrides have been reported to contain traces of the free alkali metal.[4c,17] Moreover, the reaction of cyclohexanone with sodium in the presence of trimethylsilyl chloride is reported to give a mixture consisting of predominantly 1 and 2.[18] We found that reactions of cyclohexanone with different batches of sodium hydride obtained from different suppliers (in dioxane, in the presence of Me_3SiCl) produced essentially identical ratios of 1 and 2 (see Table I). Moreover, the use of sodium hydride which had been extracted with a solution of naphthalene in THF to remove traces of sodium[8c] gave the same results (see Table I). Therefore, reduction by an alkali metal impurity does not appear to be a major pathway in the formation of the alkyl trimethylsilyl ethers.

Another possible pathway for the formation of alkyl trimethylsilyl ethers involves addition of Me_3SiH (which might be formed by reduction of Me_3SiCl)[19] to the ketone (path c in Scheme III). This pathway was considered unlikely, and was ruled out by conducting the reaction of cyclohexanone with NaH and Me_3SiCl in the presence of Et_3SiH. Neither of the triethylsilyl ethers, **9** or **10**, could be detected in the product mixture. (A comparison sample of the mixture of triethylsilyl ethers **9** and **10** was prepared by treatment of cyclohexanone with sodium hydride and triethylsilyl bromide in dioxane.)



Finally, production of the alkyl trimethylsilyl ether **1** by reduction of the trimethylsilyl enol ether **2** during the reaction (path d in Scheme III) was ruled out by demonstrating the stability of **2** to the reaction conditions. When **2** was treated with NaH and Me_3SiCl in refluxing dioxane for 36 h, <0.1% of **1** could be detected by VPC.

Since trimethylsilyl chloride is known to trap alkoxides efficiently, the predominance of trimethylsilyl enol ethers in the product mixtures from the reactions of ketones with KH or NaH in the presence of trimethylsilyl chloride indicates that, under these conditions, the metal hydrides are serving primarily as bases for enolate formation, and that reduction is at most a minor side reaction. The reaction rates, at least under some of the conditions, are slower than might be expected on the basis of what is known of the reactions of ketones with NaH and KH in the absence of trimethylsilyl chloride. This in part may be a consequence of poisoning of the metal hydride surface by the trimethylsilyl chloride.[20]

Trimethylsilyl enol ethers are versatile intermediates in organic synthesis.[3h,i,j,21] The use of KH with Me_3SiCl in dioxane for the preparation of trimethylsilyl enol ethers from symmetrical ketones, ketones which can enolize in only one direction, and from unsymmetrical ketones when mixtures are desired, should have some preparative value. The yields are competitive with those of existing methods for the preparation of these compounds, and this method is expected to be applicable to very large-scale reactions. If a few percent of alkyl silyl ether can be tolerated, this method, using NaH, has the feature of being reasonably inexpensive as well. The use of metal hydrides in the presence of trimethylsilyl chloride has potential applicability for the conversion of other compounds with acidic hydrogens into silylated derivatives.[22]

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere, and liquids were transferred with nitrogen-flushed syringes. Only *glass stoppers* were used on reaction flasks.[14] The verb "concentrated" refers to the evaporation of solvent under reduced pressure (water aspirator) using a rotary evaporator.

Vapor-phase chromatographic (VPC) analyses were performed on a Varian Aerograph Model 90-P instrument using helium as the carrier gas at a flow rate of 100 mL/min; retention times were measured relative to that of air.[23]

Infrared (IR) spectra were obtained using a Perkin-Elmer Infracord Model 137 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained using a Varian T-60 spectrometer; chemical shifts are reported in parts per million using chloroform (δ 7.24) as an internal reference.

Materials. Pentane was obtained from petroleum ether (30–60 °C) by shaking with concentrated sulfuric acid, drying over potassium carbonate, and distilling; the fraction boiling below 41.5 °C was used. Hexane was shaken with concentrated sulfuric acid, dried over potassium carbonate, and distilled from calcium hydride. Unless otherwise indicated, heptane, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from lithium aluminum hydride, and toluene and dioxane were distilled under reduced pressure from sodium and lithium aluminum hydride. Trimethylsilyl chloride (Me_3SiCl) and hexamethylphosphoric triamide (HMPA) were distilled from calcium hydride. Triethylamine was distilled from barium oxide or from calcium hydride. Lithium hydride was obtained from MC&B Chemicals, Norwood, Ohio. Sodium hydride (dispersion in mineral oil) was obtained from Alfa Inorganics, Beverly, Mass., unless otherwise indicated. Potassium hydride (slurry in mineral oil) was obtained from Alfa Inorganics.

Authentic samples of trimethylsilyl alkyl ethers **1**,[18] **5**,[24] and **7**[25] were prepared by treating the corresponding alcohols with Me_3SiCl and pyridine. A mixture of **3a**[26] and **3b**[26] [1:3 ratio by VPC (SF-96)[23]] was prepared from 2-methylcyclohexanone by reduction with lithium aluminum hydride in THF (reported to give a 1:3 ratio of cis and trans alcohols),[27] followed by treatment with Me_3SiCl and Et_3N. A sample of silyl enol ether **2**[3h,i] was prepared from cyclohexanone by treatment with Me_3SiCl and Et_3N in the presence of $ZnCl_2$.[28] A mixture of **8a**, **8b**, and **8c** [72:24:4 ratio by VPC (Carbowax)[23]] was prepared from 2-heptanone by addition to excess Ph_3CK in DME (forming the kinetic enolate; House and Trost[29] report a 54:37:9 ratio of enolate isomers prepared in this manner), followed by treatment with Me_3SiCl.[30] We thank Dr. Anne M. Hudrlik for providing samples and comparison spectra of silyl enol ethers **6**[3i] and **8**.[3i]

General Procedure. The experiments described in Table I were carried out in the following general manner. The metal hydride (30–35 mmol) was washed (except for LiH) with three 5-mL portions of pentane, and to the residue were added 15–20 mL of solvent, 0.5 g of undecane (internal standard), 30–35 mmol of Me_3SiCl, and 20–25 mmol of cyclohexanone. The mixture was heated to reflux with an oil bath. After 2 h, a 1-mL portion was withdrawn into a syringe containing 1 mL of Et_3N,[31] and the resulting mixture was added to 30 mL of water overlaid with 10 mL of ether. The aqueous phase was extracted with ether, and the combined organic layers were dried ($MgSO_4$), concentrated, and analyzed by VPC (SE-30).[23] Later samples were taken and analyzed in a similar manner.

The experiments described in Table II were carried out in an analogous manner, except that 2-methylcyclohexanone was used; in most runs decane was present as an internal standard, but the relative detector response for decane and the products was not calculated.

Preparation of 1-(Trimethylsiloxy)cyclohexene (2) using KH. Potassium hydride (5.35 g of a 30% slurry in oil, 40 mmol) was washed with five 10-mL portions of pentane; to the residue were added 30 mL of dioxane, 6.0 mL (5.1 g, 47 mmol) of trimethylsilyl chloride, and 2.46 g (25 mmol) of cyclohexanone, and the resulting mixture was heated at reflux for 7 h. Workup as usual (ether)[33] and distillation yielded 3.35 g (79%) of silyl ether **2** as a colorless liquid, bp 77–80 °C (24 mm) [lit.[3i] bp 74–75 °C (20 mm)].[34,35] VPC analysis (SF-96,[23] column temperature 135 °C; under these conditions *n*-undecane had a retention time of 7.3 min) showed peaks at 1.0 (dioxane, 0.1%), 2.6 (cyclohexanone or cyclohexanol, 0.1%), 4.7 (**1**, 0.1%), and 5.9 min (**2**, 99.7% of peak area).

Preparation of Trimethylsilyl Enol Ethers (4a,b) of 2-Methylcyclohexanone Using KH. Potassium hydride (7.74 g of a 22% slurry in oil, 42 mmol) was washed with three 20-mL portions of pentane; to the residue were added 20 mL of dioxane, 5 mL (4.28 g, 39 mmol) of trimethylsilyl chloride, and 3.26 g (29 mmol) of 2-methylcyclohexanone, and the resulting mixture was heated at reflux for 11 h. Workup as usual (ether)[33] and distillation yielded 4.297 g (80%) of a mixture of silyl ethers **4a** and **4b** as a colorless liquid, bp 73–77 °C (14 mm) [lit.[3i] bp 90–93 °C (20 mm)].[34b,35] VPC analysis (SF-96,[23] column temperature 115 °C; under these conditions *n*-undecane had a retention time of 13.4 min) showed peaks at 0.3 (0.8%), 1.7 (0.1%), 5.6 (2-methylcyclohexanone, 0.8%), 10.5 (**3a**, 4.7%), 11.5 (**3b**, 1.2%), 12.4 (**4a**, 58.6%), and 15.3 min (**4b**, 33.8% of peak area). The NMR integration indicated a 3:2 ratio of **4a** and **4b**.

Preparation of 1-(Trimethylsiloxy)-1-phenylethene (6) Using NaH. Sodium hydride (2.85 g of a 57% dispersion in oil, 68 mmol) was washed with 20 mL of pentane; to the residue were added 40 mL of dioxane, 9 mL (7.7 g, 71 mmol) of trimethylsilyl chloride, and 5.08 g (42 mmol) of acetophenone, and the resulting mixture was heated at reflux for 20 h. Workup as usual (pentane)[33] and distillation yielded 7.23 g (89%) of silyl ether **6** as a colorless liquid, bp 91–97 °C (10 mm) [lit.[3i] bp 89–91 °C (12 mm)].[34] VPC analysis (SF-96,[23] column temperature 160 °C; under these conditions *n*-undecane had a retention time of 11.8 min) showed peaks at 0.9 (dioxane 0.2%), 5.2 (acetophenone, 3.3%), 7.1 (**5**, 7.7%), and 11.5 min (**6**, 88.8% of peak area).

Preparation of Trimethylsilyl Enol Ethers (8a,b,c) from 2-Heptanone Using KH. Potassium hydride (5.75 g of a 50% slurry in oil, 72 mmol) was washed with two 20-mL portions of pentane; to the residue were added 40 mL of dioxane, 9 mL (7.7 g, 71 mmol) of trimethylsilyl chloride, and 4.25 g (37 mmol) of 2-heptanone, and the resulting mixture was heated at reflux for 13 h. Workup as usual (ether)[33] and distillation yielded 5.39 g (78%) of a mixture of silyl ethers **8a**, **8b**, and **8c** as a colorless liquid, bp 74–81 °C (19 mm) [lit.[3i] bp 94–95 °C (52 mm)].[34] VPC analysis (SF-96,[23] column temperature 130 °C) showed peaks at 1.7 (dioxane, 0.1%), 4.6 (2-heptanone, 2.3%), 10.2 (**7**, 1.3%), 10.4, 11.9, and 12.8 (unresolved, **8a,b,c**, 96.3% of peak area), and 29.6 min (0.1% of peak area). VPC (Carbowax)[23] indicated that **8a**, **8b**, and **8c** were formed in a 53:33:14 ratio.[30] The NMR integration indicated a 4:2:1 ratio of **8a**, **8b**, and **8c**.

Treatment of Cyclohexanone with NaH and Et_3SiBr. Sodium hydride (1.1 g of a 57% dispersion in oil, 26 mmol) was washed with three 5-mL portions of pentane; to the residue were added 20 mL of dioxane, 3 mL (3.42 g, 17 mmol) of triethylsilyl bromide, and 1.24 g (13 mmol) of cyclohexanone, and the resulting mixture was heated at reflux for 6 h. Workup as usual (ether)[33] and distillation yielded 2.68 g (100% as **10**) of a mixture of $Et_3SiOSiEt_3$, **9**,[18] and **10**[18] as a colorless liquid; bp 120–123.5 °C (16 mm) [for **10**, lit.[18] bp 113–114 °C (16 mm)]; IR (film) 6.00, 6.90, 7.37, 7.96, 8.13, 8.42 (strong), 9.36 (strong), 9.86 (strong), 9.99 (strong), 10.15, 11.27 (strong), 12.05 (strong), and 13.4 μm (strong); NMR (CCl_4) δ 0.33–2.17 (br, 40 H), 4.75

(m, 1 H); VPC analysis (SE-30,[23] column temperature 145 °C) showed major peaks at 9.6 ($Et_3SiOSiEt_3$ and **9**, 22% of peak area) and 12.2 min (**10**, 78% of peak area).

Registry No.—**1**, 13871-89-1; **2**, 6651-36-1; **3a**, 39789-14-5; **3b**, 39789-19-0; **4a**, 19980-33-7; **4b**, 19980-35-9; **5**, 14856-75-8; **6**, 13735-81-4; **7**, 53690-75-8; **8a**, 19980-26-8; **8b**, 19980-30-4; **9**, 4419-18-5; **10**, 4342-22-7; $Et_3SiOSiEt_3$, 994-490; triethylsilyl bromide, 1112-48-7; NaH, 7646-69-7; Me_3SiCl, 75-77-4; KH, 7693-26-7.

References and Notes

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(9) Combinations of sodium hydride with various transition-metal salts behave as reducing agents toward a number of functional groups; see J. J. Brunet and P. Caubère, *Tetrahedron Lett.*, 3947 (1977), and references cited therein; see also B. Loubinoux, R. Vanderesse, and P. Caubère, *ibid.*, 3951 (1977).

(10) In view of the work described here and in view of previous results [J. C. Powers, R. Seidner, T. G. Parsons, and H. J. Berwin, *J. Org. Chem.*, **31**, 2623 (1966)], the reaction of KH with dimethylformamide to yield dimethylamine after hydrolysis (ref 4c) is probably a deprotonation (and decarbonylation) rather than a reduction of the carbonyl group as originally suggested.

(11) In the presence of 18-crown-6, KH is reported to be soluble in THF to the extent of about 2×10^{-5} M: E. Buncel and B. Menon, *J. Am. Chem. Soc.*, **99**, 4457 (1977). The pK_a of H_2 was estimated to be 35.3.

(12) Me_3SiCl has been used as a scavenger for alkoxides in acyloin reactions: K. Rühlmann, *Synthesis*, 236 (1971), and references cited therein; see also J. J. Bloomfield, D. C. Owsley, and J. M. Nelke, *Org. React.*, **23**, 259 (1976).

(13) McConaghy and Bloomfield (ref 7c) have studied the reactions of ketones with sodium hydride in the presence of methyl iodide. Ketones which were resistant to enolization gave mixtures of products resulting from reduction (followed by O-alkylation), mono- and di-C-alkylation, and C-alkylation followed by reduction (and O-alkylation), while cyclopentanone gave predominantly C-alkylation with only 0.5% reduction. Earlier, House and Kramar (ref 3d) reported the reactions of two ketones with sodium hydride in the presence of methyl iodide to give only mixtures of C-alkylated products.

(14) In some of our early small-scale runs, employing sodium hydride in THF, the reactions were somewhat faster than those described here and *reduction* (giving 1) predominated. Control experiments established that these abnormal reactions were obtained only when rubber septa were used, and all subsequent reactions were carried out in glass-stoppered flasks.

(15) The cause of the solvent effects has not been established. Perhaps the reaction of Me_3SiCl with the metal hydride is accelerated by the more polar solvents, and the surface of the hydride becomes coated with metal halide.

(16) Other workers have stated that attempts to prepare trimethylsilyl enol ethers by reacting ketones with NaH[3i] or KH[4c] in the presence of trimethylsilyl chloride (exact conditions not specified) were unsuccessful. These reports are not necessarily at variance with our results, since we find that such reactions are very slow in a number of common solvents (e.g., THF, DME).

(17) In the reaction of 1-phenyl-2-propanone with NaH,[3j] the small amounts of reduction product which were occasionally formed were attributed to traces of Na in certain lots of NaH.[3j]

(18) K. Rühlmann, A. Sitzki, and C. Michael, *Chem. Ber.*, **101**, 285 (1968).

(19) Me_3SiCl is reduced to Me_3SiH by NaH in the presence of dipolar aprotic solvents such as HMPA; A. J. Chalk, *J. Organomet. Chem.*, **21**, 95 (1970); see also H. Jenkner, *Chem. Ztg.*, **85**, 264 (1961).

(20) Other workers have observed instances where Me_3SiCl diminishes the apparent reactivity of NaH[8c] and KH.[4a,c] See also ref 16.

(21) For reviews on the chemistry of silyl enol ethers, see (a) P. F. Hudrlik, in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, 1976, pp 127–159; (b) J. K. Rasmussen, *Synthesis*, 91 (1977).

(22) We have briefly investigated the reactions of butyraldehyde and of γ-butyrolactone with NaH and KH in the presence of Me_3SiCl. Mixtures of products were obtained, and these reactions did not appear to be of preparative value (P. F. Hudrlik, J. M. Takacs, and D. T. Chou, unpublished work). The reactions of carboxylic acids with NaH/Me_3SiCl in THF have been used to prepare acyloxysilanes: I. Kuwajima, T. Sato, N. Minami, and T. Abe, *Tetrahedron Lett.*, 1591 (1976) (see footnote 6 therein).

(23) The following VPC columns were used: SE-30, 10% SE-30 on Chromosorb W, 10 ft × 0.25 in. aluminum; SF-96, 10% SF-96 on Chromosorb W, 20 ft × 0.25 in. aluminum; Carbowax, 25% Carbowax 20M on Chromosorb W, 20 ft × 0.25 in. aluminum.

(24) W. Gerrard and K. D. Kilburn, *J. Chem. Soc.*, 1536 (1956).

(25) W. J. Richter and D. H. Hunnemann, *Helv. Chim. Acta*, **57**, 1131 (1974).

(26) (a) T. Nishishita, M. Yoshihara, and S. Oshima, *Shitsuryo Bunseki*, **20**, 347 (1972); *Chem. Abstr.*, **78**, 83483u (1973); (b) T. Nishishita, M. Yoshihara, and S. Oshima, *Maruzen Sekiyu Giho*, **No. 17**, 60 (1972); *Chem. Abstr.*, **79**, 17654v (1973).

(27) H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965); see also ref 3b, p 63.

(28) (a) Belgian Patent 670 769 (1966); *Chem. Abstr.*, **65**, 5487d (1966); (b) A. Bazouin, J. Dunogues, and M. Lefort, French Patent 1 436 568 (1966); *Chem. Abstr.*, **66**, 18764z (1967).

(29) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 1341 (1965).

(30) The order of elution (**8a** first, **8c** last) on VPC (Carbowax)[23] was the same as that reported by House and co-workers.[3i]

(31) Triethylamine was used to prevent hydrolysis of the silyl ethers on aqueous workup. See ref 3h, 21a, and 32.

(32) P. F. Hudrlik, Ph.D. Thesis, Columbia University, New York, N.Y., 1968.

(33) The reaction mixture was cooled to room temperature, triethylamine was added (1 equiv/equiv of silyl halide used),[31] and the resulting mixture was poured into water overlaid with pentane or ether. The layers were separated, the aqueous phase was extracted with four or five portions of the same solvent, and the combined organic layers were dried ($MgSO_4$) and concentrated.

(34) The IR and NMR spectra of this sample (a) corresponded to those of an authentic sample, and (b) were in agreement with data reported for this compound.

(35) The IR spectrum of this sample was very similar to that shown for this compound in ref 32.