

hexane (Alfa Inorganics) in 2 mL of dry methylene chloride was added 0.11 mL (1.0 mmol) of *tert*-butyl mercaptan at 0 °C under nitrogen. The mixture was stirred and allowed to warm to room temperature over a 15–20-min period. The ester or lactone (0.5 mmol) in 0.25 mL of dry methylene chloride was added and the mixture was stirred at room temperature under nitrogen until TLC indicated that the reaction had gone to completion (usually 4–24 h). The reaction mixture was quenched by addition of ether followed by careful addition of 3% hydrochloric acid. The organic layer was washed with 5% sodium hydroxide solution and brine, dried over MgSO₄, and evaporated to dryness to afford a viscous oil.

All products prepared this way were found by TLC and NMR to be essentially pure upon evaporation of solvent, except for compounds 13 and 14 which were purified by preparative TLC on silica gel PF₂₅₄. Isolated yields of products are given in Table I for several examples.

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Supplementary Material Available: IR, NMR, and mass spectral data for compounds 8–16 (1 page). Ordering information is given on any current masthead page.

Registry No.—5, 60699-27-6; trimethylaluminum, 75-24-1; *tert*-butyl mercaptan, 75-66-1.

References and Notes

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- (8) Yields are of essentially pure crude products except for entries 13 and 14 which were purified by preparative TLC.

Oxidation of Trialkylsilyl Enol Ethers via Hydride Abstraction: a New Procedure for Ketone to Enone Conversion¹

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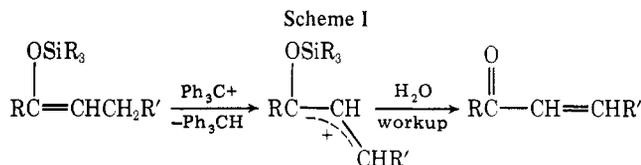
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The conversion of ketones into enones is often a transformation of great synthetic utility and interest. Much recent effort has engendered several methods to replace the classical bromination–dehydrobromination³ and direct dehydrogenation⁴ schemes. These new methods generally involve formation of the α -phenylseleno⁵ or α -methylthio^{6a} (or α -phenylthio^{6b}) ketones from an enolate derivative of the starting ketone followed by the thermal elimination of the selenic or sulfenic acid. These two-step procedures require milder conditions and afford higher yields than do the classical methods. We wish now to report an alternative to the above methods, namely the direct oxidation of the trialkylsilyl enol



ether of the ketone by vinylogous hydride abstraction with trityl tetrafluoroborate and other hydride-abstracting reagents.

This new procedure is based on the oxidation technique we developed recently involving the treatment of trimethylsilyl, *tert*-butyl, and trityl ethers of alcohols with trityl salts to afford ketones and aldehydes.⁷ We anticipated the sequence of events shown in Scheme I when this reaction was applied to silyl enol derivatives, namely allylic hydride abstraction to afford an oxygenated allylic cation which upon workup would furnish the enone. The results of the application of this scheme to the ketone to enone conversion are shown in Table I.

For example, when the trimethylsilyl enol ether 1 of cyclohexanone was oxidized by trityl salt, cyclohexenone 2 was produced in yields ranging from 30 to 70% (entries 1–6). This reaction was used to test several different methods for oxidation via hydride abstraction. The first, method A, involved treatment of the silyl enol ether 1 with commercially available⁸ trityl tetrafluoroborate in dichloromethane solution at 25 °C. Method B utilized the generation of the trityl cation from trityl methyl ether⁹ and boron trifluoride etherate in dichloromethane solution at 25 °C. With both methods excess collidine was used as a cosolvent in some cases. A third procedure, method C, was identical to method B except that acetonitrile was used as solvent. The final technique employed, method D, involved the use of dichlorodicyanoquinone (DDQ) in benzene at 25 °C. In all of the above methods, the reactions were conducted under a nitrogen atmosphere.

The results of Table I indicate that methods A and B proved to be the best in general, usually affording much higher yields than the others. Either of these two methods could give higher yield with a given substrate and therefore no clear choice between them could be made. In nearly all cases oxidation was incomplete; i.e., some starting ketone was always obtained upon aqueous workup. Longer reaction times or additional equivalents of the hydride-abstracting reagent did not significantly improve the yield of the desired enones.

Examination of the results with the two isomeric enol silyl ethers 4 and 6 prepared from 2-methylcyclohexanone indicates the regiospecificity of the method. The more highly substituted enol derivative 4 afforded only 2-methylcyclohexenone 5 (entries 7 and 8), whereas the less substituted enol ether 6 furnished only 6-methylcyclohexenone 7 (entries 9 and 10). The enol silyl ether 8 prepared from 2,6-dimethylcyclohexanone was oxidized to 2,6-dimethylcyclohexenone 9 with less than 10% of the exocyclic α -methylene ketone being formed (entries 11–13). This oxidation procedure has also been successfully applied to cyclopentanone (entries 14–17), acyclic ketones (entries 18 and 19), and esters (entries 20 and 21), although the yields are somewhat lower in these cases.

In the ketone to enone conversion, the use of a trialkylsilyl derivative of the ketone is a necessity. This requirement is underscored by the fact that similar enol ether derivatives are not oxidized under our conditions. For example, the triphenylsilyl enol ether 22 and the ethyl enol ether 23 of cyclo-

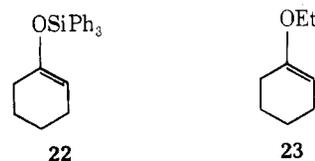


Table I. Hydride Abstraction—Oxidation of Trialkylsilyl Enol Derivatives

Entry	Silyl derivative	Registry no.	Product ^a	Registry no.	Method ^b	Time, h	Oxidant/ether ^c	Yield, % ^d enone/ ketone
(1)		6651-36-1		930-68-7	A	0.5	2	64/34
(2)	1		2		A/collidine	2	1.5	70/28
(3)	1		2		B	0.5	1	45/40
(4)	1		2		C	0.5	1	30/25
(5)	1		2		D	1	1.5	28/6
(6)		62791-22-4	2		B	0.5	1	35/5
(7)		19980-35-9		1121-18-2	A	1	2	63/27
(8)	4		5		B	0.5	1	42/30
(9)		19980-33-7		6610-21-5	A	2	2	75/23
(10)	6		7		B	0.5	1	42/20
(11)		63547-53-5		40790-56-5	A	1	2	60/18 ^e
(12)	8		9		B	0.5	1	65/20
(13)	8		9		B/collidine	0.5	1	85/0
(14)		11980-43-9		930-30-3	A	1	2	50/15
(15)	10		11		A	2	2	49/19
(16)	10		11		B	0.5	1	20/15
(17)	10		11		D	1	1.5	10/5
(18)		55339-64-5		3212-68-8	A	1	2	45/35
(19)		63547-54-6		4643-25-8	B	0.5	1	23/0
(20)		63547-55-7		638-10-8	B	0.5	1	10/0
(21)		31469-16-6		97-63-2	A	0.5	1	50/0
(22)		13735-81-4		5326-01-2	A	0.5	1	60

^a Products were identified by comparison (NMR, IR, VPC retention time) with authentic samples. ^b Method A: Ph₃C⁺ BF₄⁻ in CH₂Cl₂ at 25 °C under N₂; method B: Ph₃COMe and BF₃OEt₂ in CH₂Cl₂ at 25 °C under N₂; method C: Ph₃COMe and BF₃OEt₂ in CH₃CN at 25 °C under N₂; method D: DDQ in PhH at 25 °C under N₂. ^c Ratio of the oxidant or hydride abstractor (Ph₃CX or DDQ) to the trialkylsilyl enol ether derivative. ^d Yields were determined by vapor-phase chromatographic analysis of the reaction mixture after workup using either tetralin (Methods A and D) or pentadecane (methods B and C) as the internal standard. Separate experiments showed that tetralin was not oxidized to any great extent by trityl salt within 2 h under the conditions of methods A or D. Pentadecane is totally stable to these conditions. ^e At most, 5–10% of the exocyclic α-methylene ketone is formed, as shown by VPC analysis.

hexanone both gave no oxidation under the conditions of method B. For the ester to α,β -unsaturated ester transformation, it is known that simple dialkyl ketene acetals, analogous to the alkyl trialkylsilyl ketene acetals **16** and **18**, can be oxidized to α,β -unsaturated esters with trityl salts.¹⁰

When the trimethylsilyl enol ethers lack a hydrogen in the allylic position β to the oxygen atom, as is the case with the enol ether **20** prepared from acetophenone, the reaction with trityl salt takes a different course. Nucleophilic attack by the electrons of the enol ether on the trityl cation is now observed and the α -tritylated ketone **21**¹¹ is obtained in 60% yield (entry 22). However, in all cases of silyl enol ethers having β allylic protons, this alternative pathway of nucleophilic attack is less favored than hydride abstraction, and oxidation is the predominant reaction course.

Since trialkylsilyl enol derivatives can be easily prepared regiospecifically from ketones¹² and esters¹³ in high yields, this procedure should prove quite useful for the facile introduction of unsaturation into these molecules.

Experimental Section

General. All of the trialkylsilyl enol ethers were prepared by literature procedures.¹² The trimethylsilyl ketene acetals were prepared by our previously described method.¹³ The procedure of Rutherford was used to prepare trityl methyl ether.⁹ Trityl tetrafluoroborate was purchased from Aldrich Chemical Co. and Cationics, Inc. The triphenylpropionophenone **21** displayed physical properties identical to those reported.¹¹

General Oxidation Procedure. The following are typical experimental procedures for each method.

Method A. In a 25-mL round-bottom flask, 0.497 g (1.5 mmol) of trityl tetrafluoroborate, 0.148 g (1.2 mmol) of collidine, and 0.051 g of tetralin as an internal VPC standard were dissolved with stirring in 10 mL of dichloromethane (freshly distilled from calcium hydride and stored over molecular sieves) at 25 °C under a nitrogen atmosphere. To this was added 0.170 g (1 mmol) of the trimethylsilyl enol ether of cyclohexanone **1**, and the solution was stirred. After the indicated period of time, the reaction mixture was quenched with water and analyzed by VPC (10% carbowax 20M on 60–80 mesh Chromosorb W, $\frac{1}{8}$ in. \times 6 ft column). In the case of **1**, after 2 h VPC analysis indicated a mixture of 70% cyclohexenone and 28% cyclohexanone. For 2,6-dimethylcyclohexanone, a different column was used for VPC analysis (20% carbowax 20M on 60–80 mesh Chromosorb W $\frac{1}{8}$ in. \times 11 ft column).

Method B and C. A 50-mL round-bottom flask equipped with septum inlet, mercury relief valve, and magnetic stirring was flushed with nitrogen and immersed in a water bath at 25 °C. The flask was charged with 1.37 g (5 mmol) of trityl methyl ether and 10 mL of dichloromethane (or acetonitrile). Boron trifluoride etherate, 0.94 g (6.66 mmol) was injected all at once. After 10 min of stirring, 1-trimethylsilyloxycyclohexene (**1**) 0.844 g (5 mmol) was added dropwise over a 5-min period. After an additional 30 min, the reaction mixture was quenched by addition of 3 mL of 1 M potassium carbonate in water. Pentadecane was added as internal VPC standard, and after separation and drying (anhydrous MgSO₄) analysis of the organic phase (20% carbowax 20 M on 60–80 mesh Chromosorb W, $\frac{1}{4}$ in. \times 6 ft column) established the presence of cyclohexenone (2.3 mmol, 45%) together with recovered cyclohexanone (2.0 mmol, 40%).

Method D. In a 25-mL round-bottom flask were dissolved 0.340 g (1.5 mmol) of dichlorodicyanoquinone (DDQ) and 0.051 g of tetralin as an internal standard in 10 mL of benzene with stirring at 25 °C under a nitrogen atmosphere. To this was added in one portion 0.176 g (1 mmol) of the trimethylsilyl enol ether of cyclohexanone **1**. After 1 h, the reaction mixture was quenched with water. VPC analysis (using the same column as for method A) indicated 28% cyclohexenone and 6% cyclohexanone.

Separate experiments showed that tetralin was not oxidized to any great extent by trityl salt or DDQ within 2 h under the conditions of methods A and D.

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Registry No.—cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 2,6-dimethylcyclohexanone, 2816-57-1; cyclopentanone, 120-92-3; 2,4-dimethylpentan-3-one, 565-80-0; trityl tetrafluoroborate, 341-02-6; trityl methyl ether, 596-31-6; boron trifluoride etherate, 109-63-7; dichlorodicyanoquinone, 84-58-2.

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Reduction of Organic Compounds with the Hydroxyborohydride Ion

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The hydroxyborohydride ion, BH₃OH⁻, is formed during the hydrolysis of the borohydride ion, BH₄⁻.^{1,2} In the reduction of esters by aqueous borohydride solutions, Kirsch and Lee³ observed an increase in the rate of reduction when the borohydride solutions were allowed to age before adding the esters, and they proposed that the increased reducing power of the aged solutions was due to the formation of the BH₃OH⁻ ion. By use of a quenching flow reactor described in a previous publication,⁴ it is possible to prepare alkaline solutions containing the BH₃OH⁻ ion in concentrations as high as 0.35 M. The half-life of BH₃OH⁻ in such solutions is 3.9 h at 20 °C and pH \geq 12.5. To determine the utility of the BH₃OH⁻ ion as a reducing agent, we have studied the reduction of esters, nitriles, nitro compounds, ketones, and alkyl halides.