(9) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, 1969, Chapter 4-2.

(10) One feature of the shifted spectrum suggests that even in 3 the europium may not be coordinated symmetrically with the carbonyl oxygen. At a 1:1 mole ratio of shift reagent/substrate the C-2 methylene protons are nicely separated to two doublet of doublets spread out over 1 ppm, whereas the ω (C-6) methylenes form a much narrower band (0.4 ppm) and appear as a triplet (in the unshifted spectra the peaks due to these two methylenes have nearly equal widths, 0.15 and 0.20 ppm, respectively).

(11) P. Chamberlain and G. H. Whitham, *J. Chem. Soc. B*, 1131 (1969).

(12) R. Noyori and M. Kato, *Bull Chem. Soc. Jpn.*, **47**, 1460 (1974).

Preparation of *tert*-Butyl Thioesters

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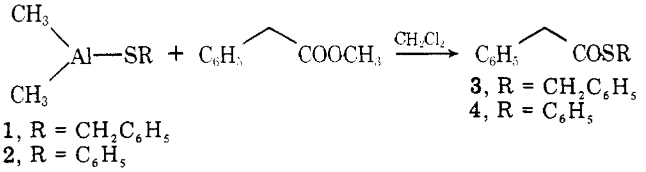
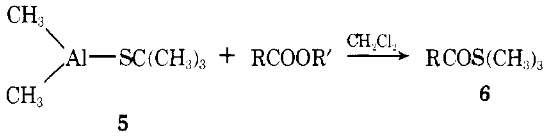
There has been considerable interest recently in activating carboxyl groups for the purpose of synthesizing macrocyclic lactones.[2] Masamune et al.[3a] have described a method of carboxyl activation using *tert*-butyl thioesters. These workers have developed preparations of *tert*-butyl thioesters from the corresponding acid chlorides or mixed anhydrides and thallous 2-methylpropane-2-thioate.[3] It has been reported that diethylaluminum ethanethiolate will open propiolactone and butyrolactone to the ω-hydroxy ethyl thioesters.[4] Corey briefly reported in 1973[5,6] that the aluminum reagents **1** and **2**, prepared from trimethyl aluminum and the corresponding mercaptan, react with methyl phenylacetate to produce the thioesters **3** and **4**, respectively, in good yield. We have found that the corresponding *tert*-butyl reagent **5**, prepared in situ from trimethyl aluminum and *tert*-butyl mercaptan in methylene chloride, reacts with a variety of functionalized methyl and ethyl esters at room temperature to produce *tert*-butyl thioesters **6**. We believe that this method of preparation may have some advantages over Masamune's procedures.[3] The method avoids using toxic thallium reagents and often the methyl and ethyl esters are more readily available than the acids or acid chlorides. In addition, reagent **5** is a very mild Lewis acid whereas Masamune's reagent systems are basic. Thus, for base-sensitive compounds, the aluminum thioate method might be preferable in the synthesis of *tert*-butyl thioesters.

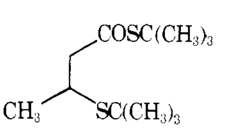


1, $R = CH_2C_6H_5$
2, $R = C_6H_5$
3, $R = CH_2C_6H_5$
4, $R = C_6H_5$



5 6

In Table I are shown isolated yields for a number of representative esters which have been converted to the corresponding *tert*-butyl thioesters. In general, the rate of reaction for ethyl and methyl esters is nearly identical. Ethyl crotonate, on treatment with **5**, gave a mixture of products, **6** and **7**, resulting from 1,4-addition of *tert*-butyl mercaptan to the double bond. Similar results were obtained with both dimethyl fumarate and ethyl cinnamate. Thus, it appears that α,β-unsaturated esters will generally give conjugate addition products with reagent **5**.



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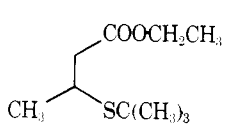

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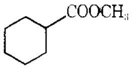
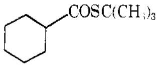
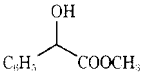
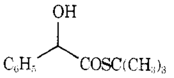
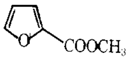
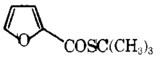
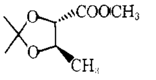
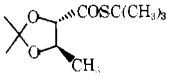
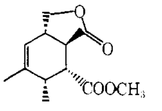
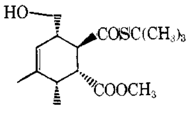
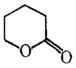
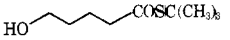
Lactones also react with reagent **5** to produce ω-hydroxy *tert*-butyl thioesters. The rate of reaction of **5** with γ-lactones is considerably faster than the rate of reaction with methyl esters, as can be seen from the example in Table I. δ-Valerolactone is readily converted to the hydroxy *tert*-butyl thioester on treatment with **5**.

Experimental Section

General Procedure for Preparation of *tert*-Butyl Thioesters. To a solution of 0.4 mL (1.0 mmol) of 2.5 M trimethyl aluminum in

Table I. Synthesis of *tert*-Butyl Thioesters from Methyl and Ethyl Esters and Lactones[8]

Starting ester	Registry no.	*tert*-Butyl thioester	Compd no.	Registry no.	Isolated yield, %
$C_6H_5COOCH_3$	93-58-3	$C_6H_5COSC(CH_3)_3$	8[7]	13291-44-6	90
$C_6H_5COOCH_2CH_3$	93-89-0	$C_6H_5COSC(CH_3)_3$	8[7]		95
$CH_3(CH_2)_{16}COOCH_2CH_3$	111-61-5	$CH_3(CH_2)_{16}COSC(CH_3)_3$	9	33563-87-0	100
$C_6H_5CH_2COOCH_2CH_3$	101-97-3	$C_6H_5CH_2COSC(CH_3)_3$	10	61049-77-2	80
	4630-82-4		11[3]	54829-37-7	80
	771-90-4		12	63599-51-9	90
	611-13-2		13	63599-52-0	75
	63640-49-3		14	63599-53-1	85
	63599-50-8		15	63599-54-2	90
	542-28-9		16	63599-55-3	60

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 $MgSO_4$, 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 PF_{254}. Isolated yields of products are given in Table I for several examples.

Acknowledgment. We are indebted to the National Institutes of Health (HL-18450) for financial support and to Dr. A. Basha for obtaining mass spectra.

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

(1) Fellow of the A. P. Sloan Foundation, 1975–1979; Recipient of a Career Development Award from the National Institutes of Health, 1975–1980 (HL-00176).
(2) K. C. Nicolaou, *Tetrahedron Rept.*, 683 (1977), for a review of the subject.
(3) (a) S. Masamune, S. Kamata, and W. Schilling, *J. Am. Chem. Soc.*, **97**, 3515 (1975); (b) S. Masamune, S. Kamata, J. Diakur, Y. Sugihara, and G. S. Bates, *Can. J. Chem.*, **53**, 3693 (1975).
(4) T. Hirabayashi, K. Itoh, S. Sakai, and Y. Ishii, *J. Organomet. Chem.*, **25**, 33 (1970).
(5) E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, **95**, 5830 (1973); E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, 925 (1975).
(6) Cf. S. Warwel and B. Ahlfaenger, *Chem.-Ztg.*, **101**, 103 (1977).
(7) For previous syntheses of this *tert*-butyl thioester see: J. W. Kimball and E. E. Reid, *J. Am. Chem. Soc.*, **38**, 2757 (1916); H. Rheinboldt, F. Mott, and E. Motzkus, *J. Prakt. Chem.*, **134**, 257 (1932).
(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 Conversion[1]

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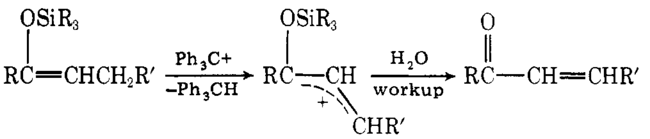
The conversion of ketones into enones is often a transformation of great synthetic utility and interest. Much recent effort has engendered several methods to replace the classical bromination–dehydrobromination[3] and direct dehydrogenation[4] schemes. These new methods generally involve formation of the α-phenylseleno[5] 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.

Scheme I



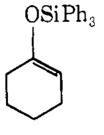
This new procedure is based on the oxidation technique we developed recently involving the treatment of trimethylsilyl, *tert*-butyl, and trityl ethers of alcohols with trityl salts to afford ketones and aldehydes.[7] We anticipated the sequence of events shown in Scheme I when this reaction was applied 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 available[8] trityl tetrafluoroborate in dichloromethane solution at 25 °C. Method B utilized the generation of the trityl cation from trityl methyl ether[9] 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-



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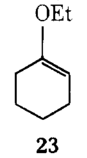

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