1360, 1240, 1160, 1040; NMR (CCl_4) 5.4 (m, 1 H), 2.4 (m, 2 H), 2.0 (s, 3 H), 1.75–1.95 (m, 3 H), 1.65 (m, 3 H), 1.2–1.6 (m, 4 H), 0.9 (s, 3 H), 0.85 (s, 3 H); mass spectrum, m/e 194 (M^+)] and α-ionone: 3%; RRT 1.00. The second fraction consisted of 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-ol: 8%; bp 138 °C (18 mm) [lit.[12] bp 130–132 °C (13 mm)]; IR (neat) 3350, 1460, 1130, 1080, 980, 950, 820, 740; NMR ($CDCl_3$) 5.3 (m, 1 H), 3.75 (m, 1 H), 2.3 (s, 1 H, OH), 1.8–2.2 (m, 3 H), 1.7 (m, 3 H), 1.25–1.6 (m, 6 H), 1.15 (d, J = 6 Hz, 3 H), 0.94 (s, 3 H), 0.88 (s, 3 H); mass spectrum, m/e 196 (M^+).

Entry 5. Column chromatography gave two fractions eluted respectively with 97/3 hexane–ether and 9/1 hexane–ether. The former contained 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-one (5%). GC analysis of the latter fraction (A, 130 °C) revealed the presence of 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-ol (60%; RRT 0.93) and of 4-(2,6,6-trimethylcyclohex-1-yl)butan-2-ol: 28%; RRT 1.00; bp 130 °C (13 mm) [lit.[13] bp 90 °C (0.2 mm)]; IR (neat) 3350, 1460, 1380, 1130, 1080; NMR ($CDCl_3$) 3.7 (m, 1 H), 2.4 (s, 1 H, OH), 1.1–1.5 (m, 12 H), 1.15 (d, 3 H), 0.9 (m, 9 H); mass spectrum, m/e 180 ($M^+ - H_2O$).

β-Ionone (Entry 6). GC (A, 175 °C) analysis showed 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)butan-2-one [79%; RRT 0.89; bp 126 °C (20 mm) [lit.[11] bp 125 °C (18 mm)]; IR (neat) 1720, 1360, 1160; NMR (CCl_4) 2.3 (m, 2 H), 2.05 (s, 3 H), 1.55 (s, 3 H), 1.3–2.1 (8 H), 1.0 (s, 6 H); mass spectrum, m/e 194 (M^+)] and β-ionone: 2%; RRT 1.00.

(*R*)-Carvone (Entry 7). The product distribution was established through GC analysis (B, 140 °C) of five fractions obtained by spinning-band distillation of the crude hydrogenated mixture in the temperature range 101–108 °C (20 mm). Three fractions contained single components with a 75–85% purity. 2-Methyl-5-(1-methylethyl)cyclohexanone: 14%; RRT 0.50; bp 101–102 °C (20 mm); IR (neat) 1715, 1450, 1370, 1320, 1220; NMR (CCl_4) 2.0–2.5 (m, 3 H), 1.3–1.9 (m, 6 H), 0.7–1.05 (m, 9 H); mass spectrum, m/e 154 (M^+), 111 ($M^+ - C_3H_7$). 2-Methyl-5-(1-methylethenyl)cyclohexanone: 24%; two peaks, corresponding to epimers at C_2 (RRT 0.61 and 0.66 and area ratio of 55/45); bp 104–105 °C (20 mm); IR (neat) 3090, 1715, 895; NMR (CCl_4) 4.7 (m, 2 H), 2.35 (m, 3 H), 1.3–2.1 (5 H), 1.7 (s, 3 H), 0.95 (m, 3 H); mass spectrum, m/e 152 (M^+), 95 ($M^+ - C_4H_9$). 2-Methyl-5-(1-methylethyl)-2-cyclohexen-1-one: 34%; RRT 0.81; bp 106–107 °C (20 mm) [lit.[14] bp 100–102 °C (14 mm)]; IR (neat) 3040, 1675, 1450, 1430, 800; NMR (CCl_4) 6.75 (m, 1 H), 2–2.6 (m, 4 H), 1.3–2.0 (5 H), 0.95 (t, 6 H); mass spectrum, m/e 152 (M^+), 82 ($M^+ - C_5H_8$). Starting ketone: 20%; RRT 1.00.

6-Methyl-2,4-heptanedione (Entry 9). Starting dione (8%) and 6-methyl-2-hydroxy-4-heptanone [47%; bp 99 °C (20 mm) [lit.[15] bp 90 °C (12 mm)]; IR (neat) 3430, 1715, 1460, 1405, 1370, 1120, 1030, 940; NMR ($CDCl_3$) 4.15 (m, 1 H), 3.5 (s, 1 H, OH), 2.5 (d, 2 H), 2.25 (m, 2 H), 1.0–1.3 (m, 1 H), 1.15 (d, 3 H), 0.9 (d, 6 H); mass spectrum, m/e 144 (M^+), 129 ($M^+ - CH_3$), 126 ($M^+ - H_2O$)] were separated by column chromatography (hexane–ether, 9/1). GC analysis (B, 140 °C) of the fraction containing the ketol revealed the presence of a second component (3% on the basis of area ratio, RRT 1.15) probably due to the isomeric 6-methyl-4-hydroxy-2-heptanone.

Entry 10. Vacuum distillation afforded 6-methyl-2,4-heptanediol: 55%; bp 118 °C (20 mm); IR (neat) 3340, 1460, 1360, 1150, 1120; NMR ($CDCl_3$) 4.5 (s, 2 H, OH), 3.95 (m, 2 H), 0.95–2.0 (5 H), 1.2 (d, 3 H), 0.9 (d, 6 H); mass spectrum, m/e 128 ($M^+ - H_2O$), 89 ($M^+ - C_4H_9$).

Registry No. 1, 5392-40-5; 2, 24190-29-2; 3, 7059-50-9; 4, 3002-23-1; 5, 39721-65-8; 6, 13720-37-1; 7, 59471-80-6; 8 (isomer 1), 6909-25-7; 8 (isomer 2), 5524-05-0; 9, 33375-08-5; 1,1-diethoxy-3-octyne, 79328-69-1; 1-hexyne, 693-02-7; 1,1-diethoxy-2-bromoethane, 2032-35-1; 1,1-diethoxyoctane, 54889-48-4; (*E*)-1,1-diethoxy-3-octene, 79328-70-4; (*Z*)-1,1-diethoxy-3-octene, 79328-71-5; 3,7-dimethyl-6-octen-1-ol, 106-22-9; 3,7-dimethyloctan-1-ol, 106-21-8; 4-(2,6,6-trimethylcyclohex-1-yl)butan-2-ol, 3293-47-8; β-ionone, 14901-07-6; 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)butan-2-one, 17283-81-7; 6-methyl-2-hydroxy-4-heptanone, 59357-17-4; 6-methyl-4-hydroxy-2-heptanone, 57548-36-4; 6-methyl-2,4-heptanediol, 79356-95-9; 1-hexyn-3-ol, 105-31-7; 1-hexen-3-ol, 4798-44-1; 3-hexanol, 623-37-0; 5-decyne, 1942-46-7; decane, 124-18-5; (*Z*)-5-decene, 7433-78-5; (*E*)-5-decene, 7433-56-9; 5-dodecyn-7-ol, 74835-62-4; 6-dodecanol, 6836-38-0; (*Z*)-5-dodecen-7-ol, 79313-71-6; (*E*)-5-dodecen-7-ol, 79313-72-7; diphenylacetylene, 501-65-5; 1,2-diphenylethane, 103-29-7; (*Z*)-1,2-diphenylethene, 645-49-8; (*E*)-1,2-diphenylethene, 103-30-0; ethyl phenylpropynoate, 2216-94-6; ethyl 3-phenylpropanoate, 2021-28-5; ethyl (*Z*)-3-phenylpropenoate, 4610-69-9; ethyl (*E*)-3-phenylpropenoate, 4192-77-2; 1-decyne, 764-93-2; 1-decene, 872-05-9; 1-octene, 111-66-0; octane, 111-65-9; (*E*)-2-octene, 13389-42-9; (*Z*)-2-octene, 7642-04-8; 1-methoxy-4-nitrobenzene, 100-17-4; 1-methoxy-4-aminobenzene, 104-94-9; 2-undecanone, 112-12-9; 2-undecanol, 1653-30-1; 1-phenyl-1-propanone, 93-55-0; 1-phenyl-1-propanol, 93-54-9; phenylacetonitrile, 140-29-4; β-phenylethylamine, 64-04-0; bis(β-phenylethyl)amine, 6308-98-1; 3,7-dimethyl-6-octen-1-al, 106-23-0; Ni, 7440-02-0.

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(13) Zink, M. P.; Ehrenfreund, J.; Wolf, H. R. *Helv. Chim. Acta* **1974**, *57*, 1116.
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Preparation and Properties of (2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl Chloride and (2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl Enol Ethers

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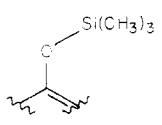
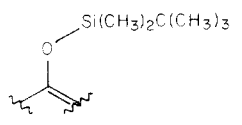
Received June 25, 1981

(2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl chloride (TPS chloride, **3**) is an inexpensive and readily prepared silylating agent for ketones. A variety of silyl enol ethers **4** were obtained by reaction of **3** with ketones. The acid- and base-catalyzed rates of hydrolysis of **4** were examined and compared to the rates for the corresponding trimethylsilyl and *tert*-butyldimethylsilyl enol ethers.

Since House first described a general synthesis of trimethylsilyl enol ethers **1** from trimethylchlorosilane and ketones,[1] these compounds have been shown to be useful enolate equivalents for the synthesis of enones,[2] α-hydroxy



1



2

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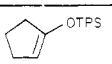
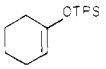
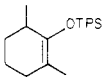
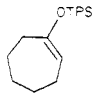
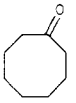
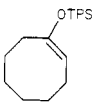
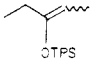
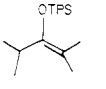
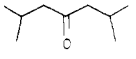
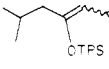
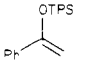
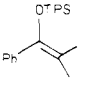
(2) (a) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011. (b) Ryu, I.; Murai, S.; Hatayama, Y.; Sonoda, N. *Tetrahedron Lett.* **1978**, 3455. (c) Jung, M. E.; Pan, Y.; Rathke, M. W.; Sullivan, D. F.; Woodbury, R. P. *J. Org. Chem.* **1977**, *42*, 3961.

0022-3263/81/1946-5348$01.25/0

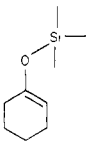
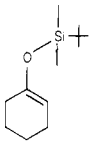
Table I. Formation of TPS Enol Ethers

ketone	reaction time,[a] h	product	mp, °C	% yield[b]
	1	 4a	66-68	88
	1	 4b	69.5-70.5	91
	8	 4c	87.5-88.5	81
	1.5	 4d	51-52	92
	2	 4e	65.5-67	91
	1.5	 4f	oil	73[c]
	6	 4g	74-75	95
	6	 4h	oil	86[c]
	3	 4i	96-96.5	87
	6	 4j	85-86	81

[a] Reaction times are not optimized. [b] Yield of isolated product after purification. [c] Mixture of *E* and *Z* isomers.

ketones,[3] 1,4-diketones,[5] and other functionalized carbonyl compounds.[6] Their utility is sometimes limited by their susceptibility to hydrolysis, but this problem may be overcome by use of the *tert*-butyldimethylsilyl derivatives **2**.[7] *tert*-Butyldimethylsilyl chloride, however, is considerably more expensive than trimethylsilyl chloride.[8] We

Table II. Hydrolysis of Silyl Enol Ethers

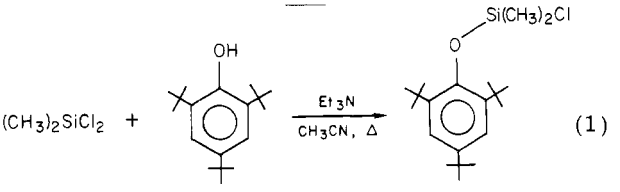
silyl enol ether	hydrolysis conditions[a]	reaction time, h	% ketone[b]
 5	A	1	20
	A	6	100
	B	0.25	100
	C	1	<5
 6	A	1	0
	A	6	0
	B	0.25	80
	B	1	100
	C	1	0
 4b	A	1	0
	A	6	0
	B	0.25	10
	B	1	70
	B	2	100
	C	1	0
	D	1	100

[a] A, HOAc/THF/H_2O, 1:10:1; B, THF/1 M HCl(aq), 20:1; C, THF/1 M NaOH, 20:1; D, KF on Celite (1:1), 2 M in CH_3CN. Reaction mixtures with solutions A-C are homogeneous. [b] Determined by GLC with an internal standard (see Experimental Section).

attempted to prepare a silylating reagent which would provide hydrolytic stability similar to that of the *tert*-butyldimethylsilyl group at a more reasonable cost. We now report the synthesis of (2,4,6-tri-*tert*-butylphenoxy)dimethylsilyl chloride (TPS chloride, **3**), a reagent which fulfills the above requirements.

Results and Discussion

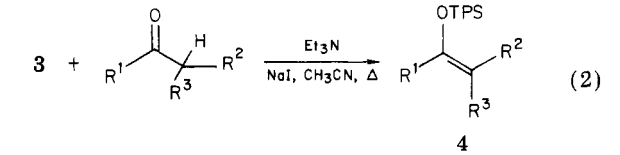
The reaction of dichlorodimethylsilane with 2,4,6-tri-*tert*-butylphenol gives TPS chloride in 93% yield (eq 1).



(1)

3 (93%)

TPS chloride is a white crystalline solid which is stable to dry air and has been kept in a desiccator for several months without decomposition or discoloration. Its utility as a silylating reagent was demonstrated by reaction with several ketones[9] (eq 2, Table I). The reaction gives TPS



(2)

4

enol ethers **4** in good yields, and most of these derivatives

(3) Brook, A. G.; Macrae, D. M. *J. Organomet. Chem.* **1974**, *77*, C19. Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319. Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3427.

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(5) Kobayashi, Y.; Taguchi, T.; Tokuno, E. *Tetrahedron Lett.* **1977**, 3741.

(6) For excellent reviews on silyl enol ether syntheses and reactions, see: Rasmussen, J. K. *Synthesis* **1977**, *2*, 91. Fleming, I. *Q. Rev., Chem. Soc.* **1981**, 83.

(7) Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4462 and references cited therein.

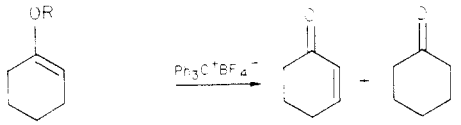
(8) Current Aldrich Chemical prices: trimethylsilyl chloride, approximately $6.80/mol; *tert*-butyldimethylsilyl chloride, approximately $162/mol. *tert*-Butyldimethylsilyl chloride may be prepared by the method of Corey[15] at a cost of approximately $80/mol. In contrast, TPS chloride costs about $20/mol to prepare.

(9) Cazeau, P.; Moulines, F.; Laporte, O.; Duboudin, F. *J. Organomet. Chem.* **1980**, *201*, C9. These authors provided the basic procedure for silyl enol ether synthesis. Olah, G. A.; Narang, S. G.; Gupta, B. G. B.; Malhota, R. *J. Org. Chem.* **1979**, *44*, 1247. These authors provide some insight on mechanistic aspects of a similar silylating agent.

are crystalline solids which may be stored without protection from air or moisture for several months without deterioration.

The rate of hydrolysis of TPS enol ethers under a variety of conditions was investigated by using the cyclohexanone derivative **4b** (Table II). The hydrolysis of the trimethylsilyl (**5**, Table II) and *tert*-butyldimethylsilyl (**6**, Table II) derivatives was examined under the same conditions for comparison. The results are summarized in Table II. It is clear that the TPS enol ether not only is more resistant to acid hydrolysis than the trimethylsilyl derivative but also is more resistant than the *tert*-butyldimethylsilyl derivative. Both **4b** and **6** are stable to base treatment. Finally, the TPS group may be removed completely within 1 h by using KF on Celite.[10]

As an example of the utility of TPS enol ethers we investigated the trityl fluoroborate oxidation of silyl enol ethers **4b**, **5**, and **6** to enones[2c] (eq 3).



(3)

4b, R = TPS	91%	6%
5, R = SiMe$_3$	64%	34%
6, R = Si-*t*-BuMe$_2$	35%	5%

Reaction of **5** with trityl fluoroborate gave 2-cyclohexene-1-one and cyclohexanone in 64% and 34% yields, respectively.[2c] Similarly, reaction of **6** gave 2-cyclohexene-1-one (35%) and cyclohexanone (5%).[2c] Presumably, cyclohexanone is formed in these reactions by protonation of silyl enol ether by an intermediate acid. The TPS derivative **4b** reacted in 10 min to give a 91% yield of 2-cyclohexen-1-one and only 6% of cyclohexanone.

We are currently investigating the full scope of the trityl fluoroborate oxidation and other reactions of TPS enol ethers.

Experimental Section

Acetonitrile, triethylamine, and all ketones were distilled from calcium hydride before use and stored under argon. Acetonitrile, triethylamine, acetophenone, and sodium iodide[11] were obtained from Fisher Chemical. 3-Pentanone and 2,6-dimethyl-4-heptanone were obtained from Matheson Coleman and Bell. All other ketones, 2,4,6-tri-*tert*-butylphenol, and dichlorodimethylsilane (distilled before use) were obtained from Aldrich. Trimethylsilyl- and *tert*-butyldimethylsilyl enol ethers were prepared by the method of Cazeau.[9] Trityl tetrafluoroborate was prepared by the method of Dauben.[12] All reactions were carried out under an argon atmosphere. Gas chromatographic data were obtained on a Varian 920 chromatograph equipped with a 4 ft × 0.25 in. column packed with 15% SE-30 on acid-washed Chromsorb P. ^{1}H NMR spectra were recorded on Bruker WM-250 and Varian T-60 spectrometers with $CDCl_3$ as the solvent and are reported in parts per million relative to Me_4Si. Infrared spectra were taken on a Perkin-Elmer 237 B spectrometer with $CHCl_3$ as the solvent and a polystyrene standard. Low-resolution mass spectra were obtained with a Finnegan 4000 GC/MS. High-resolution mass spectra were obtained with a Varian CH-5 double-focusing mass spectrometer at the Michigan State University Department of Biochemistry Mass Spectrometry Facility. Elemental analyses were performed by the Spang Microanalytical Laboratory. Melting points are uncorrected. Yields of silyl enol ethers are not maximized.

(2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl Chloride (3). 2,4,6-Tri-*tert*-butylphenol (131 g, 0.5 mol), triethylamine (84 mL, 0.6 mol), and dichlorodimethylsilane (67 mL, 0.55 mol) were dissolved in 500 mL of acetonitrile and refluxed overnight. The reaction mixture was then allowed to cool to ambient temperature and concentrated in vacuo. The residue was dissolved in 500 mL of pentane and washed with water (3 × 100 mL). The solution was dried with $MgSO_4$, decolorized with Norit-A, and filtered through Celite. The clear, lightly colored solution was concentrated to dryness, giving 165 g (93%) of **3** as white crystals: mp 79–81 °C; NMR δ 7.28 (s, 2 H), 1.44 (s, 18 H), 1.30 (s, 9 H), 0.73 (s, 6 H); IR 2945, 1420, 1260, 1200, 1120 cm^{-1}; mass spectrum, *m/e* 354 (M$^+$), 339, 303. The crystals may be recrystallized from heptane, giving white needles melting at 80–81 °C. We found that this last step was unnecessary for subsequent use of **3** to prepare silyl enol ethers. Anal. Calcd for $C_{20}H_{35}OSiCl$: C, 67.66; H, 9.94; O, 4.51; Cl, 9.99; *m/e* 354.2146. Found: C, 67.68; H, 10.05; O, 4.34; Cl, 9.85; *m/e* 354.2152.

General Procedure for Preparation of TPS Enol Ethers (4). TPS Enol Ether of Acetophenone (4i). Acetophenone (2.92 mL, 25 mmol), triethylamine (6.3 mL, 37.5 mmol), sodium iodide (4.95 g, 27 mmol), and TPS chloride (8.9 g, 25 mmol) were dissolved in 25 mL of acetonitrile and refluxed for 3 h. After cooling to ambient temperature, the mixture was diluted with 50 mL of pentane, and washed with water (2 × 25 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by either bulb to bulb distillation or recrystallization[13] from hexanes, giving 9.9 g (86%) of **4i** as white crystals: mp 96–96.5 °C; NMR δ 7.05–7.67 (m, 7 H), 4.90 (d, 1 H, J = 2.5 Hz), 4.45 (d, 1 H, J = 2.5 Hz), 1.43 (s, 18 H), 1.28 (s, 9 H), 0.43 (s, 6 H); IR 1665 cm^{-1} (C=C); mass spectrum,[14] *m/e* 439 (M + 1), 423, 383. Anal. Calcd for $C_{24}H_{33}O_2Si$: C, 76.66; H, 9.65; O, 7.29; Si, 6.40; *m/e* (M − 57) 381.2250. Found: C, 76.56; H, 9.71; O, 7.02; Si, 6.46; *m/e* (M − 57) 381.2237.

By use of the same procedure, the following TPS enol ethers were prepared.

TPS enol ether of cyclopentanone (4a): 8.8 g (88%); white crystals; mp 66–68 °C; NMR δ 7.25 (s, 2 H), 4.68 (m, 1 H), 1.2–2.4 (m, 6 H), 1.44 (s, 18 H), 1.29 (s, 9 H), 0.39 (s, 6 H); IR 1645 cm^{-1} (C=C); mass spectrum, *m/e* 402 (M$^+$), 387, 331, 303, 247, 75, 57; high-resolution mass spectrum, calcd *m/e* 402.2954, obsd *m/e* 402.2959.

TPS enol ether of cyclohexanone (4b): 9.5 g (91%); white crystals; mp 69.5–70.5 °C; NMR δ 7.25 (s, 2 H), 4.88 (m, 1 H), 1.2–2.1 (m, 8 H), 1.43 (s, 18 H), 1.29 (s, 9 H), 0.37 (s, 6 H); IR 1665 cm^{-1} (C=C); mass spectrum, *m/e* 416 (M$^+$), 401, 360, 345, 303, 155, 75, 57. Anal. Calcd for $C_{26}H_{44}O_2Si$: C, 74.94; H, 10.64; O, 7.68; Si, 6.73; *m/e* 416.3111. Found: C, 75.08; H, 10.69; O, 7.79; Si, 6.88; *m/e* 416.3141.

TPS enol ether of 2,6-dimethylcyclohexanone (4c): 9.0 g (81%); white crystals; mp 87.5–88.5 °C; NMR δ 7.26 (s, 2 H), 1.2–2.2 (m, 7 H), 1.57 (s, 3 H), 1.45 (s, 18 H), 1.30 (s, 9 H), 1.06 (d, 3 H, J = 6.8 Hz), 0.36 (s, 3 H), 0.28 (s, 3 H); IR 1680 cm^{-1} (C=C), mass spectrum, *m/e* 444 (M$^+$), 387, 303, 75, 57. Anal. Calcd for $C_{28}H_{48}O_2Si$: C, 75.61; H, 10.88; O, 7.19; Si, 6.31; *m/e* 444.3424. Found: C, 75.41; H, 10.78; O, 7.14; Si, 6.38; *m/e* 444.3421.

TPS enol ether of cycloheptanone (4d): 9.9 g (92%); white crystals; mp 51–52 °C; NMR δ 7.25 (s, 2 H), 5.01 (t, 1 H, J = 6.7 Hz), 1.2–2.3 (m, 10 H), 1.43 (s, 18 H), 1.29 (s, 9 H), 0.36 (s, 6 H); IR 1650 cm^{-1} (C=C); mass spectrum, *m/e* 430 (M$^+$), 415, 373, 303, 169, 75, 57; high-resolution mass spectrum, calcd *m/e* 430.3267, obsd *m/e* 430.3278.

TPS enol ether of cyclooctanone (4e): 10.1 g (91%); white crystals; mp 65.5–67 °C; NMR δ 7.25 (s, 2 H), 4.77 (t, 1 H, J = 8.4 Hz), 1.2–2.3 (m, 12 H), 1.44 (s, 18 H), 1.29 (s, 9 H), 0.36 (s, 6 H); IR 1660 cm^{-1} (C=C); mass spectrum, *m/e* 444 (M$^+$), 429, 387, 336, 321; high-resolution mass spectrum, calcd *m/e* 444.3424, obsd *m/e* 444.3461.

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(11) The sodium iodide was flame dried under vacuum immediately before use.
(12) Dauben, H. J.; Honnen, R. L; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.
(13) The phenol is apparently the only impurity and is nearly completely removed by either process. However, yields from recrystallization are about 20% lower owing to the high solubility of TPS enol ethers in most solvents.
(14) Chemical ionization (CH_4) was used in this case to observe the molecular ion. All other mass spectra were done by electron-impact ionization.
(15) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

TPS enol ether of 3-pentanone (4f): 7.4 g (73%); oil consisting of *E* and *Z* isomers; bp 120 °C (0.2 torr); NMR (partial) δ 4.63 (q, J = 6 Hz) and 4.55 (q, J = 6 Hz) *E* and *Z* vinyl H; IR 1670 cm^{-1} (C=C); mass spectrum, m/e 404 (M^+), 389, 347, 319, 303, 143, 75, 57; high-resolution mass spectrum, calcd m/e 404.3111, obsd m/e 404.3110.

TPS enol ether of 2,4-dimethyl-3-pentanone (4g): 10.3 g (95%); white crystals; mp 74-75 °C; NMR δ 7.26 (s, 2 H), 2.87 (m, 1 H, J = 6.6 Hz), 1.68 (s, 3 H), 1.66 (s, 3 H), 1.44 (s, 18 H), 1.30 (s, 9 H), 0.98 (d, 6 H, J = 6.6 Hz), 0.30 (s, 6 H); IR 1670 cm^{-1} (C=C); mass spectrum, m/e 432 (M^+), 417, 376, 319, 303, 263, 75; high-resolution mass spectrum, calcd m/e 432.3424, obsd m/e 432.3404.

TPS enol ether of 2,6-dimethyl-4-heptanone (4h): 9.9 g (86%); oil consisting of *E* and *Z* isomers; bp ~160 °C (0.2 torr); NMR (partial) δ 4.53 (d, J = 9.9 Hz) and 4.31 (d, J = 9.8 Hz), *E* and *Z* vinyl H; mass spectrum, m/e 460 (M^+), 445, 403, 321, 303, 247, 75, 57; high-resolution mass spectrum, calcd m/e 460.3737, obsd m/e 460.3743.

TPS enol ether of isobutyrophenone (4j): 9.5 g (81%); white crystals; mp 85-86 °C; NMR δ 7.2-7.4 (m, 7 H), 1.77 (s, 3 H), 1.67 (s, 3 H), 1.45 (s, 18 H), 1.29 (s, 9 H), 0.086 (s, 6 H); IR 1660 cm^{-1} (C=C); mass spectrum, m/e 466 (M^+), 451, 409, 353, 303, 205, 131, 75, 57; high-resolution mass spectrum, calcd m/e 466.3267, obsd m/e 466.3271.

Hydrolysis studies of **4b**, **5**, and **6** were conducted by dissolving 1 mmol of silyl enol ether in 2.5 mL of solution A, B, C, or D. After the indicated time, the standard, decane, was added, 10 mL of ether was used to extract the solution (except for solution D, which was analyzed directly), and the solution was washed with H_2O (1 × 5 mL), dried with $MgSO_4$, and analyzed by GLC.

Trityl Tetrafluoroborate Oxidation of 4b. A solution of **4b** (2.08 g, 5 mmol) in 2.5 mL of CH_2Cl_2 was added dropwise to a suspension of trityl tetrafluoroborate (1.80 g, 5.5 mmol) in 2.5 mL of CH_2Cl_2 over 1 min at 25 °C. After 10 min the reaction was quenched with 10 mL of water. The CH_2Cl_2 layer was dried ($MgSO_4$) and the internal standard, *n*-hexadecane, was added. GLC analysis (4 ft × 0.25 in. column packed with 15% Carbowax 20M terephthalate on Chromsorb W) showed cyclohexenone (91%) and cyclohexanone (6%).

Acknowledgment is made to the National Science Foundation and the Dow Chemical Co. (for support of P.A.M., summer 1981) for partial support of this work.

Registry No. **3**, 79746-31-9; **4a**, 79746-32-0; **4b**, 79746-33-1; **4c**, 79746-34-2; **4d**, 79746-35-3; **4e**, 79746-36-4; (*E*)-**4f**, 79746-37-5; (*Z*)-**4f**, 79746-38-6; **4g**, 79746-39-7; (*E*)-**4h**, 79746-40-0; (*Z*)-**4h**, 79746-41-1; **4i**, 79746-42-2; **4j**, 79746-43-3; **5**, 6651-36-1; **6**, 62791-22-4; acetophenone, 98-86-2; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2,6-dimethylcyclohexanone, 2816-57-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; 3-pentanone, 96-22-0; 2,4-dimethyl-3-pentanone, 565-80-0; 2,6-dimethyl-4-heptanone, 108-83-8; isobutyrophenone, 611-70-1; cyclohexenone, 930-68-7; dichlorodimethylsilane, 75-78-5; 2,4,6-tri-*tert*-butylphenol, 732-26-3.

Mild Conversion of Carboxamides and Carboxylic Acid Hydrazides to Acids and Esters

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Received June 30, 1981

A mild and selective conversion of unsubstituted carboxamides and carboxylic acid hydrazides to the corresponding acids and esters is brought about by the use of acidic resins. Application of the procedure to several carboxamides and carboxylic acid hydrazides is described.

Although unsubstituted carboxamides are readily prepared from the corresponding methyl or ethyl esters, the conversion of carboxamides to esters is often difficult. The existing methods for this transformation, or that to the carboxylic acid, usually call for treatment with strong acid or base under conditions generally incompatible with sensitive substrates.[1,2] Although amide hydrolysis via nitrosation has been carried out under neutral conditions,[4] often the use of strong proton[5] or Lewis acids[6] is required. Likewise, hydrolysis of carboxylic acid hydrazides usually requires strongly acidic or basic media, although mild conversions to acids and esters using copper compounds have recently been described.[7] Although ion-exchange resins have been used widely as catalysts in organic synthesis and particularly in hydrolysis reactions,[8] only a single report of amide hydrolysis promoted by a resin has appeared.[9] We now report that use of acidic resins provides a mild method for conversion of unsubstituted carboxamides and carboxylic acid hydrazides to the corresponding acid or ester.

The procedure consists of combining the amide or hydrazide with a 15-fold excess (by weight) or Amberlyst 15

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