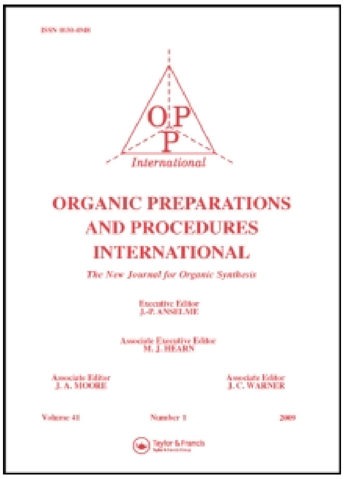

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DIRECT CONVERSION OF TRIMETHYLSILYLOXYALKANES TO ALKANOIC ESTERS

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DIRECT CONVERSION OF TRIMETHYLSILYLOXYALKANES TO ALKANOIC ESTERS

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Although other silyl compounds have been used as masking agents for alcohols,[1] trimethylsilyl (TMS) ethers ($ROSiMe_3$) remain useful.[2-4] This usefulness arises from the TMS ether's ease of preparation (chlorotrimethylsilane readily available and inexpensive), purification, desilylation, and general chemical stability. Desilylation to regenerate the alcohols has been accomplished by the action of ionic reagents in protic solvents, e.g., hydrochloric acid,[2] potassium fluoride,[3] or ammonium chloride[4] in aqueous methanol or THF and 17N acetic acid or acetic acid-THF-water (3:1:1).[1]

Some of the cited desilylation methods were incompatible with certain long-chain, multiple-unsaturated TMS ethers. Temperatures low enough to prevent degradation of the alkenic system meant slow or incomplete removal of the silyl group. The acetic acid-THF-water system[1] did smoothly transform the TMS ethers to the corresponding alcohols. Reaction times were short and the alkenic systems were unaffected. Where the desilylation was allowed to proceed for some hours, the acetate of the alcohol was formed as a by-product.

This observation led to the development of conditions for the conversion of $ROSiMe_3$ directly to ROCOR' in excellent yields without formally regenerating the alcohol. A mixture of acetic anhydride and acetic acid[5] stirred several hours with alkyl TMS ethers gave excellent conversions to acetates. Pyridine with acetic anhydride was a better solvent system but gave only partial conversions of alkyl TMS ethers to acetates. Pyridine/acetic anhydride, when used with catalytic amounts of $KF \cdot 2H_2O$, 48% HF(aq), or $BF_3 \cdot Et_2O$, completely converted the alkyl TMS ethers to acetates, did not modify the alkenic system of the original TMS ethers, and converted the alkenic TMS ethers to acetates. Esters of propionic and isobutyric acids were similarly obtained in excellent yield and purity from $ROSiMe_3$ by using the anhydride/pyridine/HF or BF_3-etherate reagent.

EXPERIMENTAL

Infrared spectra were taken of liquid films between NaCl plates on a Perkin-Elmer 137 spectrophotometer. The presence of the very sharp, strong 1252 cm^{-1} with 1256-1261 cm^{-1} inflection ($SiMe_3$) absorption coupled with the absence of the usual broad 3333 cm^{-1} (-OH) absorption was used to check the completeness of silylation. The absence of the 1252 and 3333 cm^{-1} absorptions coupled with the presence of the usual 1736-1751 cm^{-1} ester carbonyl absorption was then used to confirm the completeness of desilylation/esterification. The ethers and esters were further analyzed and identified on a 1.22 m X 0.32 cm column of base-washed Chromosorb G supporting 5% Carbowax 20M-TPA. New compounds were identified by ir and satisfactory elemental analysis (Galbraith Laboratories, Inc., Knoxville, Tenn. 37921).

Preparation of TMS Ethers (Table). The general method of Sprung and Nelson was used.[6] Ether or ether-hexane mixtures were used as solvents rather than excess pyridine. After filtration, and rinsing the precipitated pyridinium chloride, the TMS ethers were isolated by distillation of the water-washed and $MgSO_4$-dried organic layer.

Table 1.- TMS ethers $ROSiMe_3$ and $Me_3SiOROSiMe_3$ used in this study.

R	Yield (%)	bp. (°C/mm)	n_D^{25}
$-(CH_2)_4-$	55	92-3/18	1.4115[a]
$\underline{n}-C_{12}H_{25}-$	85	148-50/17-8	1.4265[b]
$\underline{n}-C_{14}H_{29}-$	77	104/0.15	1.4320[c]
$\underline{n}-C_{16}H_{33}-$	85	161/0.15	1.4347[c]
$Br(CH_2)_8-$	72	101-2/1.5	1.4501[d]

a) Ref. 7
b) Ref. 8
c) Ref. 9
d) Ref. 10

Conversion of TMS Ethers to Esters.

Survey Procedure.- A TMS ether (1.0 g) in 7-8 ml of a 4:10:1 mixture of acid anhydride/pyridine/48% HF after 5-24 hr at room temperature was treated with ice/water/$NaHCO_3$ and extracted with hexane. The extracts were then compared by glc with authentic esters. Thus, 8-bromo-1-[(trimethylsilyl)oxy]octane gave 8-bromooctyl acetate[11] free from starting material. Use of $KF{\cdot}2H_2O$ or $BF_3{\cdot}Et_2O$ gave similar results with the TMS ethers of 1-do- and tetradecanols.

Acetates.- 1-[(Trimethylsilyl)oxy]hexadecane (3 g) mixed with acetic anhydride/pyridine (2:5 v/v, 12 ml) plus 1.0 ml 48% HF, left 24 hr and poured into ice-water, gave 2.35 g (87%) of crude ester free of $SiMe_3$. Distillation at 146-8°/0.75 mm gave 2.3 g (85%) of hexadecyl acetate, 97% pure by glc.

Propionates.- Propionic anhydride/pyridine (1:3 v/v) mixed with 0.1 vol of 48% HF or $BF_3{\cdot}Et_2O$ converted the TMS ethers of 1-hexadecanol (0.1 vol) to the propionate; glc purity 99%.

Isobutyrates.- With isobutyric anhydride/pyridine (1:3 v/v) and boron trifluoride etherate (0.1 vol), the TMS ethers (0.1 vol) of 1,4-butanediol and 1-hexadecanol gave tetramethylene diisobutyrate[12] and hexadecyl isobutyrate[13]; yield and purity (glc) >95%.

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† Mention of a commercial or proprietary product in this paper does not consitute an endorsement of this product by the U.S. Department of Agriculture.

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12. Sh. G. Mikadze, Zh. Org. Khim., 1, 471 (1965), prepared this ester by a route other than pyridine/anhydride and reported n_D^{20} 1.4420; found: n_D^{25} 1.4238; bp. 70.5°/0.3 mm; IR 1739, 1393, 1348, 1261, 1198, 1161, 1081 and 755 cm^{-1}.

13. Fr. Pat. 1563259/1969 (C.A., 71, P101339) reports a preparation of this compound; found: bp. 140°/0.4; n_D^{25} 1.4383; IR 1748, 1393, 1346, 1261, 1198, 1161, 1082 and 754 cm^{-1}.

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