methoxy-3-methyl-3-(2-naphthyl)phthalide (**3**) as a colorless oil, IR absorption at 5.7 μm (five-membered lactone carbonyl). Zinc dust in alkali reduction[5] of **3** readily afforded 4-methoxy-2-(α-2-naphthylethyl)benzoic acid* (**4**), mp 176.5–177.5 °C, which by reaction[5] with CH_3Li was converted into the corresponding methyl ketone, in turn cyclized to 9-methoxy-7,12-dimethylbenz[*a*]anthracene* (**5**) mp 204.5–205.5 °C (33% overall yield from **1**), by treating with polyphosphoric acid at room temperature for 3 h.

In a similar sequence starting with **1** and methyl 1-naphthyl ketone there was obtained 10-methoxy-7,12-dimethylbenz[*a*]anthracene,[6] mp 135.0–136.0 °C, in 27% overall yield from **1**. In this case, the PPA cyclization required 40 min at 95 °C.

The application of this new synthesis to the synthesis of other methoxy- and fluoro-substituted benz[*a*]anthracenes is under study.

References and Notes

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(2) Postdoctoral Research Associate.
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(7) All new compounds marked with an asterisk gave satisfactory elemental analyses and NMR spectra.

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N-Bromosuccinimide Oxidation of Silyl Ethers[1]

Summary: N-Bromosuccinimide converts the trimethylsilyl (Me_3Si) ethers of primary alcohols into esters and the Me_3Si ethers of secondary alcohols into ketones. An aldehyde and a Me_3Si ether give a "mixed" ester in the presence of NBS.

Sir: Oxidation of alcohols is a fundamental transformation of organic chemistry which is attracting much current interest.[2] Since the hydrogens on a carbon atom attached to oxygen are labile in the free radical sense,[3] we reasoned that conversion of an alcohol into an unsymmetrical ether and treatment with *N*-bromosuccinimide (NBS) would effect the desired oxidation (eq 1).[4] In order to have the proper regiochemistry,

$$RR'CHOH \rightarrow RR'CHOR'' \xrightarrow{NBS} [RR'CBrOR''] \rightarrow RCOR' \quad (1)$$

R″ cannot possess α hydrogens and thus might be *tert*-butyl;[5] however, treating the *tert*-butyl ether of 1-hexanol with NBS under a variety of conditions gives only traces of hexanal and *N*-chlorosuccinimide fails to react at all. In addition, neither bromine nor sulfuryl chloride causes oxidation of *tert*-butyl 1-hexyl ether.

We decided to examine the analogous trimethylsilyl (Me_3Si) ethers[6] readily available in high yield from alcohols by treatment with chlorotrimethylsilane and pyridine or triethylamine.[7a] When a Me_3Si ether is dissolved in CCl_4 and stirred with NBS under the irradiation of an ordinary sun lamp, a reaction occurs. The results with a variety of systems are summarized in Table I. Thus, the trimethylsilyl ether of 1-

Table I. Oxidation of Silyl Ethers

Reactant	Conditions	Product	Yield, g (%)[a]
$CH_3(CH_2)_5OSiMe_3$	*hν*, 0 °C, 5 h	$CH_3(CH_2)_4CO_2(CH_2)_5CH_3$	1.90 (80)
$C_6H_5CH_2OSiMe_3$	*hν*, −20 °C, 2.5 h	C_6H_5CHO	1.06 (48)
$C_6H_5CH(OSiMe_3)CH_3$	*hν*, Pyr, rt, 3.5 h	$C_6H_5COCH_3$	1.37 (76)
$CH_3(CH_2)_5CH(OSiMe_3)CH_3$	*hν*, Pyr, rt, 3.5 h	$CH_3(CH_2)_5COCH_3$	1.05 (55[b])

[a] Refers to pure, isolated products. Yields not optimized. [b] Based on 36% recovery of starting material.

Table II. Oxidation of Silyl Ethers in the Presence of Aldehydes

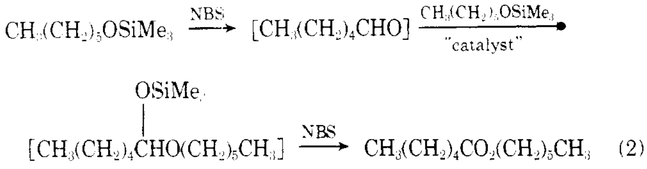
Aldehyde	Silyl ether (equiv)	Conditions	Product	Yield, g (%)
$CH_3(CH_2)_8CHO$	$CH_3CH_2OSiMe_3$ (2.0)	*hν*, 0 °C, 2.5 h	$CH_3(CH_2)_8CO_2CH_2CH_3$	0.96 (83)
$CH_3(CH_2)_4CHO$	$CH_3CH_2OSiMe_3$ (1.3)	*hν*, 0 °C, 3.5 h	$CH_3(CH_2)_4CO_2CH_2CH_3$	0.81 (58)
C_6H_5CHO	$CH_3CH_2OSiMe_3$ (1.0)	*hν*, 0 °C, 2.5 h	$C_6H_5CO_2CH_2CH_3$	0.90 (45)
C_6H_5CHO	$CH_3CH_2OSiMe_3$ (2.5)	*hν*, 0 °C, 2.5 h	$C_6H_5CO_2CH_2CH_3$	1.78 (89)
CH_3CH_2CHO	c-$C_6H_{11}OSiMe_3$ (1.0)	*hν*, 0 °C, 2.5 h	c-$C_6H_{11}O_2CCH_2CH_3$	2.72 (68)
$CH_3(CH_2)_8CHO$	$(CH_3)_3COSiMe_3$ (2.0)	*hν*, 0 °C, 2.5 h	$CH_3(CH_2)_8CO_2C(CH_3)_3$	1.28 (44)
$CH_3(CH_2)_4CHO$	$(CH_3)_3COSiMe_3$ (3.0)	*hν*, 0 °C, 2.5 h	$CH_3(CH_2)_4CO_2C(CH_3)_3$	0.97 (42)

[a] Refers to pure, isolated products. Yields not optimized.

hexanol yields the corresponding hexanoate ester in 80% yield after column chromatography.[8] Treatment of the Me_3Si ether of benzyl alcohol with NBS at −20 °C gives a 48% yield of benzaldehyde.

The silyl ethers of secondary alcohols give ketones when reacted with NBS in the presence of pyridine. For example, the Me_3Si ether of α-phenylethanol gives acetophenone in 76% yield. A 55% yield of 2-octanone is isolated from 2-(trimethylsiloxy)octane.

Isolation of an ester from the reaction employing 1-(trimethylsiloxy)hexane is a most striking result. A possible mechanism might involve the corresponding aldehyde, which is then converted to an acetal (eq 2). The failure to isolate the acetal implies that it reacts rapidly with NBS.[9] Furthermore, no hexanal was obtained so that the second step of eq 2 must be faster than the first step.[10,11]



$$CH_3(CH_2)_5OSiMe_3 \xrightarrow{NBS} [CH_3(CH_2)_4CHO] \xrightarrow[\text{"catalyst"}]{CH_3(CH_2)_5OSiMe_3} [CH_3(CH_2)_4\overset{\overset{\displaystyle OSiMe_3}{|}}{C}HO(CH_2)_5CH_3] \xrightarrow{NBS} CH_3(CH_2)_4CO_2(CH_2)_5CH_3 \quad (2)$$

Indeed, the addition of an aldehyde to a silyl ether in the presence of NBS gives the "mixed" ester (eq 3) (see Table II).

$$RCH_2OSiMe_3 + R'CHO \xrightarrow{NBS} R'CO_2CH_2R \quad (3)$$

Thus, decanal, hexanal, and benzaldehyde are each converted by NBS and the Me_3Si ether of ethanol into the corresponding ethyl esters in good yield. In addition, treatment of trimethylsiloxycyclohexane with NBS in the presence of propional gives a 68% yield of cyclohexyl propionate.

Increasing the ratio of Me_3Si ether to aldehyde improves the yield of ester. Benzaldehyde reacts with 1 equiv of trimethylsiloxyethane to give a 45% yield of ethyl benzoate. By using 2.5 equiv of the silyl ether, the yield of ethyl benzoate is improved to 89%.

This most unusual aldehyde to ester conversion can be extended to the preparation of *tert*-butyl esters. For example, decanal is transformed into *tert*-butyl decanoate in 43% yield when stirred with NBS and the Me_3Si ether of *tert*-butyl alcohol. Hexanal similarly yields *tert*-butyl hexanoate in 42% yield.

In a typical procedure, the Me_3Si ether of 1-hexanol (4.14 g, 23.7 mmol) is dissolved in 50 mL of dry CCl_4 under N_2 and cooled in an ice bath. To this is added 4.65 g (26.1 mmol, 1.1 equiv) of NBS and the reaction flask is exposed to a sun lamp for 5 h. The reaction mixture is stirred without irradiation for 3–4 h and filtered. The filtrate is stirred with $NaHCO_3$, dried, and concentrated. A benzene solution is filtered through a column of Fisher A-540 alumina (1.7 × 35 cm) to give 1.91 g (80%) of pure 1-hexyl hexanoate. In most cases, filtration through alumina was an adequate purification; however, in some systems, because of the scale used, distillation proved to be more efficient.

The mixed esterification reactions are conducted in the same way. The aldehyde and silyl ether are dissolved in CCl_4 at 0 °C. The NBS (1.1 equiv) is added and the reaction mixture is exposed to a sun lamp. When the reaction is complete, the reaction mixture is stirred for 3–4 h without light, after which workup is carried out as above.

We attempted to extend this oxidation procedure to more complex substrates; however, the presence of a double bond prevents the desired reaction. For example, the Me_3Si ether of geraniol gives only a trace of citral (not isolated) when stirred with NBS. Similarly, the Me_8Si ether of citronellol and NBS give a dark reaction mixture from which no oxidation product was obtained.

The mixed ester reaction with unsaturated substrates was equally fruitless. Citral, trimethylsiloxyethane, and NBS give a low yield (by NMR) of the corresponding ethyl ester. *trans*-Cinnamaldehyde, trimethylsiloxyethane, and NBS do not react in 4 h and give only a trace of ester after 7 days. In addition, methacrolein fails to react with the Me_3Si ether of 1-hexanol in the presence of NBS. In fact, a catalytic amount of distilled methacrolein retards the formation of 1-hexyl hexanoate in the reaction of NBS with the Me_3Si ether of 1-hexanol.

Thus, the presence of a double bond, a functional group which is known to scavenge free radicals,[12] precludes the oxidation reaction, implying that a free-radical reaction is involved. Furthermore, since a catalytic amount of methacrolein acts as an inhibitor of ester formation, a free-radical chain reaction is suggested. In addition, light is essential for the reaction since the Me_3Si ether of 1-hexanol and NBS give a very slow conversion to ester (~50% in 80 h) without a sun lamp.

It is also of interest to note that pyridine completely inhibits the conversion of primary Me_3Si ethers into esters while promoting the secondary Me_3Si ether to ketone reaction. Much work remains in exploring the mechanism of these new reactions and will be reported in due course.

In addition to its versatility as an oxidation method, this study serves as an illustration that trimethylsilyl ethers are *not inert* to NBS.

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References and Notes

(1) Presented at the 29th Southeastern Regional Meeting of the American Chemical Society, Tampa, Fla., Nov. 9–11, 1977.

(2) See, for example, R. W. Binkley, *J. Org. Chem.*, **42**, 1216 (1977), and references cited therein.

(3) M. L. Poutsma in "Methods in Free Radical Chemistry", Vol. 1, E. S. Huyser, Ed., Marcel Dekker, New York, N.Y., 1969, p 137.

(4) Indeed, two studies involving oxidation of analogous thiophenyl ethers with *N*-chlorosuccinimide appeared after initiation of the present work: (a) L. A. Paquette, W. D. Klobucar, and R. A. Snow, *Synth. Commun.*, **6**, 575 (1976); (b) P. Bakuzis, M. L. F. Bakuzis, C. C. Fortes, and R. Santos, *J. Org. Chem.*, **41**, 2769 (1976).

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(6) Trimethylsilyl ethers yield aldehydes and ketones when subjected to "hydride abstraction" by trityl tetrafluoroborate[7a] and by nitrosyl tetrafluoroborate.[7b]

(7) (a) M. E. Jung, *J. Org. Chem.*, **41**, 1479 (1976); (b) G. A. Olah and T.-L. Ho, *Synthesis*, 609 (1976).

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(9) NBS is known to oxidize acetals to esters: J. D. Prugh and W. C. McCarthy, *Tetrahedron Lett.*, 1351 (1966); L. C. Anderson and H. W. Pinnick, unpublished results.

(10) (a) In addition, since hexanal and 1-(trimethylsiloxy)hexane do not react, a "catalyst" is apparently necessary for the second step of eq 2. (b) In the case of the Me_3Si ether of benzyl alcohol, initial oxidation to benzaldehyde (presumably via the rather stable benzylic radical) must be faster than the second step so that the aldehyde and not the ester is isolated.

(11) We feel that the present data do not justify a more detailed mechanism at this time. It is of interest, however, to note the following additional observations. (a) The silicon byproduct is bromotrimethylsilane, identified by NMR (0.5 ppm) of the crude reaction mixture. (b) Bromine converts the Me_3Si ether of a primary alcohol into the ester, but is less efficient than NBS (some starting material is recovered). (c) Pyridine inhibits this bromine reaction, but a yellow solid is formed (apparently pyridine perbromide: see L. F. Fieser and M. Fieser, "Reagents For Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 966) so that the significance of this result is in doubt. (d) The Me_3Si ether of 1-hexanol fails to react with propionaldehyde in the presence of HBr so that the "catalyst" of eq 2 is not HBr.

(12) See, for example, M. E. Kuehne and R. E. Damon, *J. Org. Chem.*, **42**, 1825 (1977).

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