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(10) The dichloride **8** (X = Cl) is prepared just before use from diol **8** (X = OH) and thionyl chloride (in dry chloroform). The ionization of diol in $\mathrm{SbF_5}$–$\mathrm{SO_2ClF}$ or $\mathrm{FSO_3H}$–$\mathrm{SbF_5}$–$\mathrm{SO_2ClF}$ solutions only provides the 5-hydroxy-1-manxyl monocation, which does not further ionize to give the dication **5**. Ion **5** slowly rearranges at −45 °C to give a species whose structure is under further investigation.

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George A. Olah,* Gao Liang
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Paul v. R. Schleyer
Department of Chemistry, University Erlangen-Nurnberg
Erlangen, Germany

William Parker, C. Ian F. Watt
Department of Chemistry, University of Stirling
Stirling, Scotland

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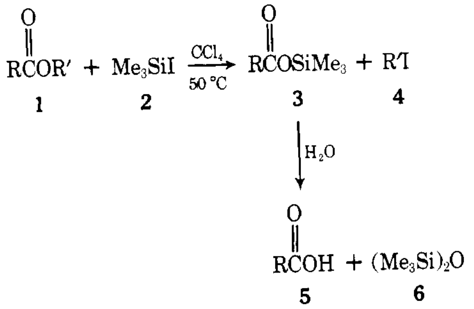
Quantitative Dealkylation of Alkyl Esters via Treatment with Trimethylsilyl Iodide. A New Method for Ester Hydrolysis

Sir:

The hydrolysis of alkyl carboxylic esters is usually carried out under acidic or basic conditions. Recently, several procedures have been developed which allow for hydrolysis under neutral conditions.[1] However, these procedures usually require the use of strong nucleophiles and high temperatures to effect dealkylation. We wish to report a very mild and extremely efficient alternative to the above methods, which proceeds in essentially quantitative yield under neutral conditions. It involves the treatment of alkyl carboxylic esters with trimethylsilyl iodide[2–4] followed by aqueous hydrolysis.

When a carboxylic ester **1** is mixed with trimethylsilyl iodide **2** in an aprotic solvent, e.g., carbon tetrachloride or deuteriochloroform, and the solution is warmed to 50 °C, a clean and efficient dealkylation occurs resulting in the formation of the trimethylsilyl carboxylate **3** and the alkyl iodide **4**. Aqueous hydrolysis of the silyl ester affords the acid **5** in essentially quantitative yield and presumably hexamethyldisiloxane **6**. For example, when a series of methyl esters **7a–l** is treated with trimethylsilyl iodide **2** in $\mathrm{CCl_4}$ at 50 °C, the corresponding silyl esters **8a–l** and methyl iodide **9** are produced in quantitative yields. The time required for the conversion varies depending on the ester and ranges from 4 h for methyl cinnamate **7e** to 35 h for methyl benzoate **7b**. A variety of other alkyl esters (ethyl, isopropyl, *tert*-butyl, benzyl, etc.) **7m–y** can also be dealkylated in quantitative yield by this process. The results for a series of esters are listed in Table I.



$$\underset{\mathbf{1}}{\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR'}} + \underset{\mathbf{2}}{\mathrm{Me_3SiI}} \xrightarrow[50\,^\circ\mathrm{C}]{\mathrm{CCl_4}} \underset{\mathbf{3}}{\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OSiMe_3}} + \underset{\mathbf{4}}{\mathrm{R'I}}$$

$$\mathbf{3} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{5}}{\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH}} + \underset{\mathbf{6}}{\mathrm{(Me_3Si)_2O}}$$

$$\underset{\mathbf{7a\text{–}l}}{\mathrm{RCO_2Me}} + \underset{\mathbf{2}}{\mathrm{Me_3SiI}} \xrightarrow[50\,^\circ\mathrm{C}]{\mathrm{CCl_4}} \underset{\mathbf{8a\text{–}l}}{\mathrm{RCO_2SiMe_3}} + \underset{\mathbf{9}}{\mathrm{MeI}}$$

We have investigated the effect of this dealkylation-hydrolysis technique upon other functionality in various ester substrates and have found it stable to a wide range of functional groups. For example, molecules containing isolated double bonds (e.g., methyl oleate **7f** and methyl linoleate **7g**), ketones (**7i**), aromatic ethers (**7j**), thioethers (**7k**), amines (**7l** and **7r**), and amides (**7s**) can all be converted into the corresponding acids in high yield without significant destruction of the additional functionality. However, $\mathrm{Me_3SiI}$ rapidly converts dialkyl ethers into alkyl silyl ethers (and thus by hydrolysis into alcohols),[5] transforms alcohols into iodides,[6] and hydrolyzes some ketals to the corresponding ketones[7] in high yields so that these functionalities are not compatible with this ester hydrolysis technique. Further studies with more functionalized molecules are currently underway to determine the effect of $\mathrm{Me_3SiI}$ on other functionality.

The possibility that the reactions we observe could be due entirely to small amounts of HI present in the $\mathrm{Me_3SiI}$ cannot be totally discounted. However, in the presence of 10–15 mole % pyridine, ester dealkylation does occur, although at a somewhat slower rate. This leads us to believe that $\mathrm{Me_3SiI}$ itself is causing dealkylation.

The possibility of selectivity between various alkyl esters toward this dealkylative hydrolysis procedure prompted us to investigate the reaction of a series of alkyl acetates and alkyl benzoates with differing alkyl groups (**7a, b, m, n, t–y**) under our conditions. From the data in Table I, it is obvious that *tert*-butyl esters and benzyl esters are rapidly dealkylated at 25 °C while with methyl, ethyl, and isopropyl esters dealkylation is very slow at 25 °C but proceeds at a moderate rate at 50 °C.[8] This would imply that *tert*-butyl and benzyl esters could be hydrolyzed selectively by this technique in the presence of the other alkyl esters, but that there would be essentially no selectivity between methyl, ethyl, and isopropyl esters at 50 °C.

We suggest a rather straightforward mechanism for this process: the ester **1** reacts with trimethylsilyl iodide **2** in a fast and reversible step to produce the silylated ester iodide salt **10** which can then go on to products (**3** and **4**) in a slow, irreversible process by either an S_N2 mechanism (R′ = Me, Et) or an S_N1 (S_Ni) mechanism (R′ = *t*-Bu, $\mathrm{CH_2Ph}$). Further mechanistic discussion will await the full paper.

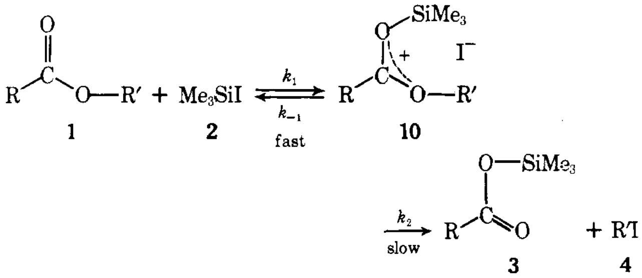
We have also made the interesting observation that when

Table I. The Dealkylation of Esters by Me3SiI

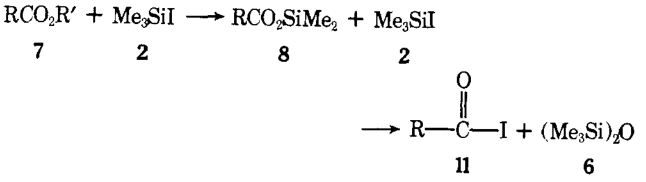
$$\underset{7}{\mathrm{RCO_2R'}} + \underset{2}{\mathrm{Me_3SiI}} \rightarrow \underset{8}{\mathrm{RCO_2SiMe_3}} + \underset{4}{\mathrm{R'I}}$$

Compound	R	R′	Temp (°C)	Solvent	Time (h)	Yield,[a] %
a	CH_3	Me	50	CCl_4	8	
b	Ph	Me	50	CCl_4	35	85
c	$CH_3(CH_2)_7$	Me	50	CCl_4	6	
d	$CH_3(CH_2)_{12}$	Me	50	CCl_4	10	
e	PhCH=CH	Me	50	CCl_4	4	
f	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$	Me	50	$CDCl_3$	8	95
g	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7$	Me	50	$CDCl_3$/pyr	20	85
h	1-Adamantyl	Me	50	$CDCl_3$	20	90
i	$CH_3CO(CH_2)_4$	Me	50	$CDCl_3$	5	84
j	2-Furanyl	Me	50	$CDCl_3$	7	
k	2-Thiophenyl	Me	50	$CDCl_3$	24	80
l	2-$NH_2C_6H_4$	Me	80	$(CH_2)_4SO_2$	1	82
m	CH_3	Et	50	CCl_4	24	
n	Ph	Et	50	CCl_4	48	
o	CH_3CH_2	Et	50	CCl_4	23	
p	$(CH_3)_2CHCH_2$	Et	50	CCl_4	21	
q	$CH_3(CH_2)_{14}$	Et	50	CCl_4	21	95
r	NH_2CH_2	Et	70	$(CH_2)_4SO_2$	48	84
s	$AcNHCH_2$	Et	50	$CDCl_3$	48	82
t	CH_3	*i*-Pr	50	CCl_4	10.5	
u	CH_3	*t*-Bu	25	CCl_4	1/6	
v	CH_3	CH_2Ph	25	CCl_4	0.5	
w	Ph	*i*-Pr	50	CCl_4	23	
x	Ph	*t*-Bu	25	CCl_4	0.5	90
y	Ph	CH_2Ph	25	CCl_4	1.5	

[a] Yields are for isolated, purified products after aqueous workup. The acids were identified by comparison (MP, NMR, IR) with authentic samples. In all cases the silyl esters are formed in quantitative yields as shown by NMR measurements.



an ester **7** is treated with excess trimethylsilyl iodide **2** for extended periods of time, the initially formed trimethylsilyl carboxylate, **8,** is slowly and efficiently converted into the acyl iodide **11** in high yield. These compounds are identified by their infrared (C=O, 1800-1830 cm^{-1}) and NMR (δ 0.8 downfield shift of CH_2 α to C=O as compared to ester) spectra and by their conversion into the corresponding acids or esters upon addition of water or alcohol. For example, treatment of ethyl palmitate **7q** with 2.5 equiv of Me3SiI for 3 days at 75 °C affords palmityl iodide **11q** in ~70% yield (by NMR).



$$\underset{7}{\mathrm{RCO_2R'}} + \underset{2}{\mathrm{Me_3SiI}} \longrightarrow \underset{8}{\mathrm{RCO_2SiMe_2}} + \underset{2}{\mathrm{Me_3SiI}}$$

$$\longrightarrow \underset{11}{\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}I}} + \underset{6}{\mathrm{(Me_3Si)_2O}}$$

Trimethylsilyl iodide **2** is prepared easily from trimethylsilyl chloride in two steps in 90% overall yield. The chloride is converted quantitatively into hexamethyldisiloxane by addition of water and base (e.g., dimethylaniline). Slow addition of 2 equiv of iodine (via solid addition funnel) to a warm (60 °C) solution of the disiloxane and 2 equiv of aluminum powder followed by reflux (1.5 h) and direct distillation affords a 90% yield of the iodide **2** as a clear water-white liquid (bp 106 °C). The compound is stable for long periods when stored in a dark, stoppered vessel under a nitrogen atmosphere at ~20 °C. Since it reacts vigorously with moisture, all transfers are done with a dry syringe. This preparation is a modification of Voronkov's original method.[2]

Additional experiments are underway to determine the full potential of this reagent. In addition to the dealkylation and hydrolysis of ethers and thioethers,[5] we are also currently investigating its reaction with amines and amides,[5] alcohols,[6] ketals, ketones, and epoxides,[7] and other functional groups.

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Michael E. Jung,* Mark A. Lyster
Contribution No. 3706, Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

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