Novel Method for Dealkylation of Esters, Ethers, and Acetals by Chlorotrimethylsilane–Sodium Iodide

By Tsuyoshi Morita,* Yoshiki Okamoto, and Hiroshi Sakurai

(*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka* 565, *Japan*)

Summary Reactions of the carboxylic esters (**1**) and the ethers (**5**) with chlorotrimethylsilane (**2**) in the presence of sodium iodide give the silyl derivatives (**3**) and (**6**) quantitatively which are easily converted into the corresponding carboxylic acids (**4**) and phenols (**7**) under mild conditions.

Recently, it was reported that iodotrimethylsilane is an effective reagent for dealkylation of esters, ethers, and acetals under neutral conditions.[1] In spite of the utility of this reagent in synthetic transformations, its applicability is limited because it must be prepared *via* two steps from chlorotrimethylsilane (**2**).[2] Ho and Olah have found that phenyltrimethylsilane–iodine is also very useful for this purpose,[3] and these results prompted us to investigate the dealkylation of the alkyl carboxylates (**1**) by using the commercially available chlorosilane (**2**) itself.

When a mixture of (**1**) (40 mmol) and (**2**) (60 mmol) was stirred in the presence of anhydrous sodium iodide (60 mmol) in acetonitrile (15 ml) at 45—75 °C for several hours, dealkylation occurred immediately and sodium chloride began to precipitate. The precipitate was filtered off to afford a solution of the corresponding trimethylsilyl carboxylates (**3**), and the reaction was monitored by n.m.r. spectroscopy. The results for several alkyl carboxylates (**3**) are in Table 1.

TABLE 1. Reaction of esters with chlorotrimethylsilane

Compound	R^1	R^2	Temp. /°C	Time /h	Yield[a] /%
(**1a**)	Me	Me	70—75	5	86
(**1b**)	"	Et	70—75	20	62
(**1c**)	"	Pr^i	70—75	35	37
(**1d**)	"	Bu^t	45	0·2	100
(**1e**)	"	CH_2Ph	45	0·5	92
(**1f**)	Pr^i	Me	70—75	9	79
(**1g**)	$Me[CH_2]_4$	Me	70—75	7	82
(**1h**)	Cyclohexyl	Me	70—75	9	86

[a] Yields were determined by n.m.r. spectroscopy for solutions in CCl_4.

$$\underset{(1)}{R^1CO_2R^2} + \underset{(2)}{Me_3SiCl} + NaI \longrightarrow \underset{(3)}{R^1CO_2SiMe_3} + R^2I + NaCl$$

The results show that for the alkyl carboxylates (**1a**—**c**), the yield of the trimethylsilyl carboxylates (**3a**—**c**) decreases with the order of bulkiness of the alkyl group R^2 ($Me > Et > Pr^i$). Dealkylation of the esters (**1d** and **e**) ($R^2 = Bu^t$, CH_2Ph) proceeds more rapidly to completion than that of the others at 45 °C. These dealkylations do not occur without sodium iodide; iodotrimethylsilane cannot be prepared by the reaction of (**2**) and sodium iodide.[4]

TABLE 2. Reaction of ethers with chlorotrimethylsilane[a]

Compound	Ar	R	Temp. /°C	Time /h	Yield[b] /%
(**5a**)	Ph	Me	70—75	27	81
(**5b**)	p-MeC_6H_4	Me	70—75	28	83
(**5c**)	Ph	CH_2Ph	50	1·5	90

[a] Conditions: ether (40 mmol), chlorosilane (60 mmol), and sodium iodide (60 mmol) in dry acetonitrile (15 ml). [b] Yields were determined by n.m.r. spectroscopy.

The silyl carboxylates (**3**), on treatment with water at room temperature, were readily converted into the corresponding carboxylic acids (**4**) and hexamethyldisiloxane.

$$(3) + H_2O \rightarrow \underset{(4)}{R^1CO_2H} + Me_3SiOSiMe_3$$

Similarly, dealkylation of the alkyl aryl ethers (**5**) by this reagent at 50—75 °C gave the corresponding aryl trimethylsilyl ethers (**6**) in 81—90% yields (Table 2). Hydrolysis of the silyl ethers (**6**) under mild conditions yielded the phenols (**7**) quantitatively (Scheme).

$$\underset{(5)}{ArOR} + (2) + NaI \rightarrow \underset{(6)}{ArOSiMe_3} + RI + NaCl$$

$$\downarrow H_2O$$

$$\underset{(7)}{ArOH} + Me_3SiOSiMe_3$$

SCHEME

In addition, the reaction of benzaldehyde dimethyl acetal (**8**) with this reagent in acetonitrile at 45 °C for 0·2 h gave benzaldehyde (**9**) quantitatively.

$$\underset{(8)}{PhCH(OMe)_2} + (2) + NaI \rightarrow \underset{(9)}{PhCHO} + MeOSiMe_3 + MeI + NaCl$$

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[3] T.-L. Ho and G. A. Olah, *Synthesis*, 1977, 417.

[4] C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 174.