

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

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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.

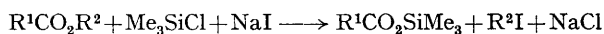
When a mixture of (1) (40 mmol) and (2) (60 mmol) was stirred in the presence of anhydrous sodium iodide (60 mmol) in acetonitrile (15 ml) at 45–75 °C for several hours, dealkylation occurred immediately and sodium chloride began to precipitate. The precipitate was filtered off to afford a solution of the corresponding trimethylsilyl

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 ₂ Ph	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 CCl₄.

carboxylates (3), and the reaction was monitored by n.m.r. spectroscopy. The results for several alkyl carboxylates (3) are in Table 1.



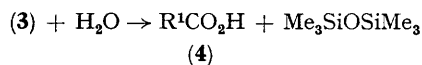
The results show that for the alkyl carboxylates (1a–c), the yield of the trimethylsilyl carboxylates (3a–c) decreases with the order of bulkiness of the alkyl group R² (Me > Et > Prⁱ). Dealkylation of the esters (1d and e) (R² = Bu^t, CH₂Ph) proceeds more rapidly to completion than that of the others 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

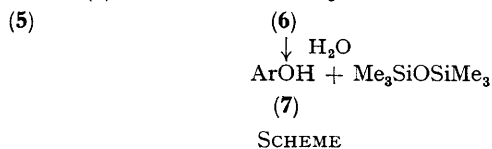
Compound	Ar	R	Temp. /°C	Time /h	Yield ^b /%
(5a)	Ph	Me	70–75	27	81
(5b)	<i>p</i> -MeC ₆ H ₄	Me	70–75	28	83
(5c)	Ph	CH ₂ Ph	50	1.5	90

^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.

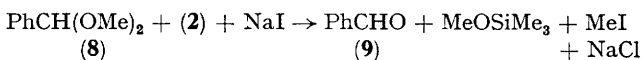
The silyl carboxylates (3), on treatment with water at room temperature, were readily converted into the corresponding carboxylic acids (4) and hexamethyldisiloxane.



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).



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.



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¹ T.-L. Ho and G. A. Olah, *Angew. Chem.*, 1976, **88**, 847; M. E. Jung and M. A. Lyster, *J. Amer. Chem. Soc.*, 1977, **99**, 968; M. E. Jung and M. A. Lyster, *J. Org. Chem.*, 1977, **42**, 3761; M. E. Jung, M. A. Andrus, and P. L. Ornstein, *Tetrahedron Letters*, 1977, 4175.

² M. G. Voronkov and Yu. I. Khudobin, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1956, 713.

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

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