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Chlorotrimethylsilane/Sodium Iodide/Zinc as a Simple and Convenient Reducing System; One-Pot Deoxygenation of Alcohols and Ethers

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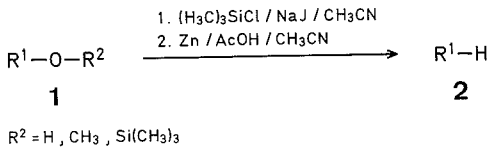
Deoxygenation of aliphatic alcohols into the corresponding alkanes is an important transformation in organic synthesis. A common route to the alkanes is reduction using various metal hydrides under anhydrous conditions[1,2]. In such a case, the process necessarily requires the initial conversion of the hydroxy function into suitable derivatives containing good leaving groups such as tosylate, mesylate, halide etc. More recently, several new methods for the one-step reduction of alcohols have been described using lithium/ammonia[3], organosilane/boron trifluoride[4], sodium borohydride/trifluoroacetic acid[5], aluminium chloride/palladium[6], diiododimethylsilane[7], and iron pentacarbonyl[8]. However, these procedures are almost limited to the α-aryl-substituted alcohols which are capable of forming relatively stable carbanions or carbenium ions. During the course of our continuing work utilizing chlorotrimethylsilane/sodium iodide reagent as an iodotrimethylsilane equivalent[9–12], we have found a novel and alternative system for one-pot conversion of alcohols and ethers **1** into the alkanes **2** via *in situ* generated iodides. The advantages of our method are as followed: (a) it is applicable to various primary and secondary alcohols, (b) the reagent, chlorotrimethylsilane/sodium iodide/zinc, is less expensive and more easily handled than other known reducing agents, (c) the reaction or work-up procedure is simple.

When the reaction of *p*-anisyl alcohol with chlorotrimethylsilane/sodium iodide was carried out in acetonitrile, followed by treatment with an excess of zinc dust[13] with stirring at 75–85 °C for 6 h, *p*-methylanisole was obtained in 61% yield by distillation after working up. A similar reaction of decyl alcohol with the reagent gave decane in 63% yield, accompanied by a considerable amount of residue in the distillation vessel. However, addition of a little acetic acid to the zinc-acetonitrile mixture in the reduction step results in a dramatic enhancement of the product yield (83% and 86% yield, respectively), owing probably to its effectiveness as a proton donor.



The results are summarized in the Table. The products were not essentially contaminated with any alkene. All alkanes were identified by comparison (N.M.R., G.L.C., b.p.) with authentic samples. On comparison with the known reducing system of alcohols via the iodides by the use of methyltriphenoxyphosphonium iodide/sodium cyanoborohydride in hexamethylphosphoric triamide[14], our present procedure is simple and convenient, producing volatile hexamethyldisiloxane as the only by-product.

On the other hand, no convenient and satisfactory route to alkanes from ethers was previously known[1]. To demonstrate further the utility of our method, we applied it for one-pot deoxygenation of alkyl or trimethylsilyl ethers **1**. Interestingly, the reaction of decyl methyl ether with chlorotrimethylsilane/sodium iodide and zinc gave decane in 82% yield. Some data for the ether reductions are also given in the Table.

Deoxygenation of Alcohols 1 (R^2 = H); General Procedure:
To a mixture of the alcohol **1** (20 mmol) and anhydrous sodium iodide (7.5 g, 50 mmol) in dry acetonitrile (20 ml), chlorotrimethylsilane (5.4 g, 40 mmol) is added dropwise with stirring over 20 min. During the addition, the reaction vessel is heated at 30–55 °C. After 0.5–2.5 h, the reaction mixture is diluted with additional acetonitrile (10 ml) and acetic acid

Table. Deoxygenation of Alcohols and Ethers **1** into Alkanes **2**

Substrate **1** R^1	R^2	Reaction 1		Reaction 2		Yield [%][a]	b.p. [°C]/torr	
		Temp. [°C]	Time [h]	Zn (equiv.)	Time [h]		observed	Lit.[15]
n-$C_{10}H_{21}$	H	30–35°	1.0	3	6.0	80	67–69°/16	57°/10
n-$C_{10}H_{21}$	H	30–35°	1.0	7	6.0	86	71–73°/20	57°/10
n-$C_{12}H_{25}$	H	30–35°	1.0	7	5.0	93	98–100°/14	91°/10
s-C_9H_{19}	H	40–45°	1.5	7	6.0	61	70–72°/54	39°/10
4-*t*-butylcyclohexyl (*cis* and *trans*)	H	50–55°	2.5	7	5.0	40[b]	59–62°/16	171°
4-H_3CO—C_6H_4—CH_2	H	30–35°	0.5	7	5.0	83	63–65°/13	176°
$(C_6H_5)_2CH$	H	30–35°	0.5	7	4.0	91	122–123°/10	125°/10
n-$C_{10}H_{21}$	CH_3	70–75°	1.5	7	4.5	82	69–71°/17	57°/10
s-C_9H_{19}	CH_3	70–75°	1.5	7	5.0	64	73–75°/60	39°/10
n-$C_{10}H_{21}$	$Si(CH_3)_3$	70–75°	1.0	6	4.0	82	70–72°/18	57°/10
4-H_3CO—C_6H_4—CH_2	$Si(CH_3)_3$	50–55°	0.5	6	5.0	81	68–69°/17	176°
$(C_6H_5)_2CH$	$Si(CH_3)_3$	50–55°	0.3	6	4.0	85	130–132°/17	125°/10

[a] Yield of isolated product of >98% purity as determined by ^{1}H-N.M.R. spectrometry and G.L.C. analysis (conditions: 1 m × 4 mm column, 5% Silicone OV-17 on Chromosorb W).
[b] Contains ~5% of 4-*t*-butylcyclohexene.

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(2 ml). Next zinc dust (3–7 equiv) is added portionwise with stirring to the resulting dark-yellow reaction mixture at room temperature. A slight evolution of heat immediately occurs and after 15 min the mixture is heated to 75–85 °C, followed by stirring vigorously for an additional 4–6 h. After cooling to room temperature, the mixture is filtered through a Büchner funnel and washed with diethyl ether (5 × 25 ml). The filtrate is washed with dilute aqueous sodium hydrogen carbonate solution (3 × 30 ml) and subsequently with aqueous sodium hydrogen sulfite solution (2 × 25 ml), then dried with anhydrous sodium sulfate. After the removal of low-boiling materials on an evaporator, the residue is distilled in vacuo to afford the pure alkane **2**.

Deoxygenation of Ethers 1 [$R^2 = CH_3$ or $Si(CH_3)_3$]; General Procedure:
A mixture of the methyl ether **1** (20 mmol), chlorotrimethylsilane (5.4 g, 50 mmol), and anhydrous sodium iodide (7.5 g, 50 mmol) in dry acetonitrile (20 ml) is heated at 50–75 °C with stirring. In the case of the trimethylsilyl ether **1** (20 mmol), chlorotrimethylsilane (3.3 g, 30 mmol) and sodium iodide (6.0 g, 40 mmol) are used in acetonitrile (20 ml). After the reaction is complete, the mixture is diluted with additional acetonitrile (10 ml) and acetic acid (4 ml). Then it is reduced with zinc and worked up in a similar manner to that described for the alcohol deoxygenation. After work-up, the pure alkane **2** is obtained by fractional distillation (column: 10 cm Vigreux).

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Electrohalomethoxylation of Chromone Derivatives

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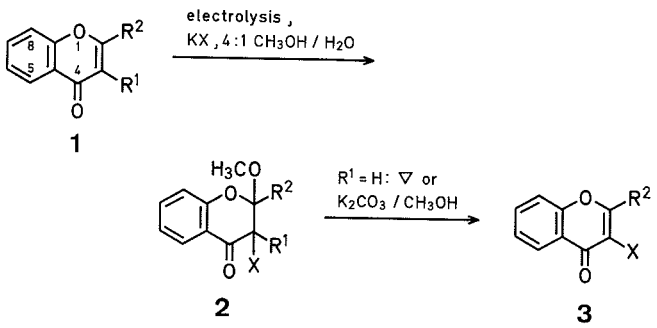
The synthetic utility of the organic electrochemistry has been generally recognized. The following conversions are note worthy: furan derivatives are converted to the corresponding 2,5-dimethoxy-2,5-dihydrofurans[1] or to ring-opened products[2], carbonyl or aromatic compounds are converted to halogenated products[3], and olefins are converted to a variety of products[4]. We now report on the electrohalomethoxylation of chromone derivatives **1**[5].



A mixture of the chromone **1** in 4:1 methanol/water containing the potassium halide as a 0.1 molar solution was electrolyzed at a graphite anode to afford the halomethoxylated product **2** in good yield (Table 1).

The chromanones **2** having a hydrogen atom at C-3 ($R^1 = H$) are unstable and decompose slowly on standing and rapidly on heating to the chromones **3**. Products **3a** and **3c** were identified by comparison with authentic samples[6]. These products **2a–d** can be converted quantitatively to **3a–d** by treatment with potassium carbonate in methanol.

This ready conversion of **2a–d** to **3a–d** is indicative that regioselective attack of halo and methoxy groups is involved in the formation of **2**. Furthermore the coupling constants ($J_{H\text{-}2,H\text{-}3} = 3$ Hz) in **2a** and **2b** suggest that the halo and methoxy groups are *cis*[7].

Many synthetic methods for chromones bearing halogen atoms at C-3 have been reported[8], but only few start from C-2 unsubstituted chromones[9]. Our electrochemical method is thus very useful to synthesize C-3 halogenated chromones.

Electrolysis of Chromones 1; General Procedure:
A mixture of the chromone **1** (1 mmol) in 4:1 methanol/water (70 ml) containing potassium halide (7 mmol) is electrolyzed in a divided cell at graphite anode under a constant current of 10 mA at room temperature for ~6 h. After 2.2 F/mol has been passed, the reaction mixture is concentrated to one-third of its original volume under reduced pressure below 40 °C and extracted with ether (40 ml). The ether layer is washed with sodium chloride solution (20 ml), dried with magnesium sulfate, and concentrated. The residue is subjected to preparative thin layer chromatography (Kieselgel 60 PF_{254}) or column chromatography (Kieselgel 60, 70–230 mesh) eluting with chloroform to afford the 3-halo-2-methoxychromanone **2** (Table 1).

3-Halochromones 3a–d; General Procedure:
A mixture of the 3-halo-2-methoxychromanone **2** (50 mg), potassium carbonate (50 mg) and methanol (5 ml) is heated at 50 °C for 2 h. The reaction mixture is poured into water (5 ml) and extracted with ether (3 × 10 ml). The ether layer is washed with sodium chloride solution (10 ml), dried with magnesium sulfate, and evaporated to give the crystalline 3-halochromone **3** quantitatively (Table 2).

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