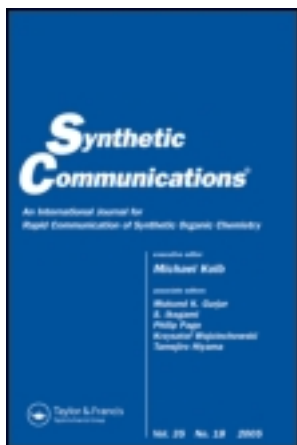


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### Trimethylchlorosilane and Water. Convenient Reagents for the Regioselective Hydrochlorination of Olefins

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**TRIMETHYLCHLOROSILANE AND WATER. CONVENIENT  
REAGENTS FOR THE REGIOSELECTIVE  
HYDROCHLORINATION OF OLEFINS.**

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**Abstract:** The hydrochlorination of a series of simple and functionalized olefins in high yields was readily accomplished using a mixture of trimethylchlorosilane and water. Hydrochlorination by this procedure is chemoselective and regioselective.

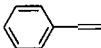
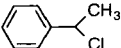






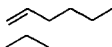
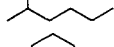















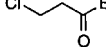
As pointed out by Kropp, hydrohalogenation is not a simple matter unless the double bond is activated by structural or electronic features.<sup>1</sup> Using surface mediated reactions, Kropp and coworkers developed greatly simplified hydrohalogenation procedures by using SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> with a variety of active halides such as

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\* To whom correspondence should be addressed.

$\text{SOCl}_2$ ,  $(\text{COCl})_2$ ,  $\text{Me}_3\text{SiBr}$ , and  $\text{PI}_3$ , that feature higher yields and improved stereo-selectivity over earlier methods.<sup>1, 2, 3</sup> They postulated that the hydrogen halide is formed via hydrolysis of the active halides by surface-bound water on the alumina or silica gel. Some of these procedures have been modified for instructional purposes.<sup>4, 5</sup>

Table 1. Hydrochlorination of Olefins Using Trimethylchlorosilane and Water.

Entry	Olefin	Product	h	yield <sup>a</sup>	Mechanism <sup>b</sup>
1			10	86%	E.A.
2			2	98%	E.A.
3			3	91%	E.A.
4			3	96%	E.A.
5			15	78% <sup>c</sup>	E.A.
6			15	70% <sup>c</sup>	E.A.
7			5	70%	E.A.
8			5	75%	E.A.
9			3	89%	N.A.
10			5	98%	N.A.
11			5	80%	N.A.
12			2	65%	N.A.
13			2	95%	N.A.

<sup>a</sup> All yields are isolated yields except for 3-chlorocyclohexanone which was measured by GC. <sup>b</sup> E.A.=Electrophilic addition<sup>6</sup>; N.A.=Nucleophilic addition<sup>7</sup>.

<sup>c</sup> Mole ratios: 5.0: 5.0: 1.0,  $\text{Me}_3\text{SiCl}$ :  $\text{H}_2\text{O}$ : olefin.

Table 2.  $^1\text{H-NMR}$  data of hydrochlorination products<sup>a</sup>

Entry	$^1\text{H-NMR}$ data ( $\delta$ )
1	1.87(d, 3H), 5.12(q, 1H), 7.22-7.51(m, 5H).
2	1.01(t, 6H), 1.50(s, 3H), 1.63-1.90(m, 4H).
3	0.95(t, 3H), 1.41-1.56(m, 2H), 1.59(s,6H), 1.70(t, 2H).
4	0.95(t, 3H), 1.41-1.56(m, 2H), 1.59(s,6H), 1.70(t, 2H).
5	1.01(t, 3H), 1.23-1.45(m, 4H), 1.50(d, 3H), 1.80(m, 2H), 4.12(m, 1H).
6	1.28-1.85(m, 6H), 2.01(br d, 4H), 3.97(m, 1H).
7	1.67(s, 6H), 3.71(s, 2H).
8	1.78(d, 3H), 2.80(d, 2H), 4.12(m, 1H).
9	2.87(t, 2H), 3.72(t, 2H).
10	2.20(s, 3H), 2.90(t, 2H), 3.70(t, 2H).
11	1.54(d, 3H), 2.19(s, 3H), 2.70(dd, $J=16$ , 6Hz, 1H), 2.96(dd, $J=16$ , 7Hz, 1H), 3.73(s,3H), 4.46(m, 1H).
12	1.70-2.41(m, 6H), 2.66(dd, $J=14$ , 6Hz, 1H), 2.84(m, 1H).
13	1.28(t, 3H), 2.78(t, 2H), 3.83(t, 2H), 4.19(q, 2H).

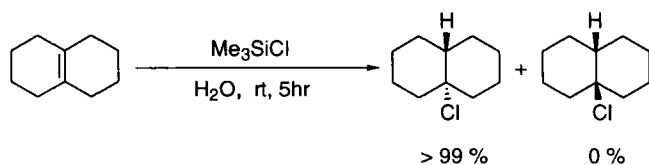
<sup>a</sup>  $^1\text{H-NMR}$ : JEOL- GSX-270MHz; solvent and reference,  $\text{CDCl}_3$

Our procedure calls for simple glassware, requires no solvent and, for most olefins, the reaction is complete within 5 h at room temperature. Product isolation is straightforward, requiring evaporation of unused trimethylchlorosilane, hexamethyldisiloxane and, when necessary, distillation of the desired product.

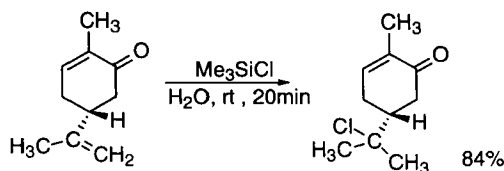
Heating the reaction mixture does not always lead to faster rates and often results in lower yields, presumably from increased vaporization of hydrogen chloride. We also found that active chlorides such as  $\text{SiCl}_4$ ,  $\text{Me}_2\text{SiCl}_2$ ,  $\text{SOCl}_2$ ,  $\text{SnCl}_4$  and  $\text{PCl}_3$  produced hydrochlorinated products in acceptable yields but that

trimethylchlorosilane was the most generally useful reagent. In this procedure, these compounds evolve hydrogen chloride at rates much faster than trimethylchlorosilane.

As shown in Table 1, regioselectivity is high. Markovnikov addition dominates for simple olefins and anti-Markovnikov addition for  $\alpha,\beta$ -unsaturated olefins. Stereochemistry was investigated using  $\Delta^{9,10}$ -octaline.<sup>8</sup> At room temperature, we obtain a trans product(>99%).<sup>9</sup> Low temperature hydrochlorination is prohibited



by the freezing of water. Chemoselectivity and regioselectivity were investigated using (R)-carvone. (5R)-5-(1-chloro-1-methylethyl)-2-methylcyclohex-2-enone<sup>10</sup> was obtained in 84% yield. Trace amounts of carvacrol are formed after 20 min. After 3 h, only carvacrol is detected in the product mixture.



**General Procedure.** In a typical experiment, a 50 mL two necked flask was charged with 4.00 mL (2.73 g, 32.4 mmol) of 3-methyl-2-pentene and mixed 0.44 mL (24.3 mmol) of water at room temperature. After briefly stirring this two phase system, trimethylchlorosilane (6.14 mL, 5.27 g, 48.6 mmol) was added by syringe. After 2 h, trimethylchlorosilane and hexamethyldisiloxane were removed

on a rotoevaporator and the residual water was taken up by sodium sulfate. The remaining liquid was distilled and identified as 3-chloro-3-methyl-pentane {bp 114-116 °C (lit.<sup>11</sup> 115-116 °C/761 torr), 98%}.

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<sup>9</sup> FT-IR(C-Cl trans : 543 cm<sup>-1</sup>), <sup>1</sup>H NMR(CDCl<sub>3</sub>, δ ): 1.1-2.2(m);

<sup>13</sup>C NMR(CDCl<sub>3</sub>, δ): 78.929, 46.452, 41.881, 28.959, 25.999, 21.930.

<sup>10</sup> <sup>1</sup>H NMR(CDCl<sub>3</sub>, δ): 1.57(d, 6H), 1.81(s, 3H), 2.1-2.8(m, 5H), 6.7(m, 1H);

<sup>13</sup>C NMR(CDCl<sub>3</sub>, δ): 199.269, 144.331, 135.188, 72.032, 47.192, 40.031, 30.492, 30.201, 27.849, 15.509.

<sup>11</sup> Beilstein, **1**,149.

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