Synthetic Methods and Reactions; XXII[1]. Hydrodehalogenation of α-Haloketones with Vanadium(II) Chloride

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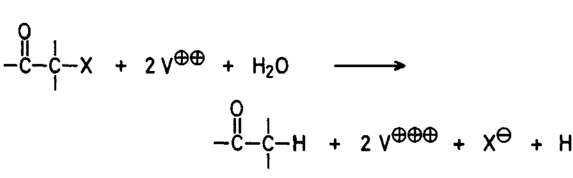
Chromium(II)[2], titanium(II), and titanium(III)[3] ions have received special attention in recent time owing to their redox potentials which are convenient for use of these ions as reagents in organic synthesis. Our effort in extending the scope of these reagents as well as developing related reducing systems led us to investigate reductions with vanadium(II) ion. The redox potential of the V(II)–V(III) couple[4],

$$V^{\oplus\oplus} = V^{\oplus\oplus\oplus} + e \quad [+0.255\,v]$$

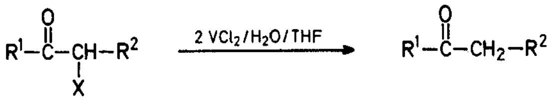
although lower than those of Cr(II)–Cr(III) [+0.41 v] and Ti(II)–Ti(III) [+0.37 v], compares favorably to the tin(II) ion: Sn(II)–Sn(IV) [−0.15 v] which has found wide application in organic synthesis.

We report herein the facile hydrodehalogenation of α-haloketones by vanadium(II) chloride[5], which proceeds according to the following stoichiometry:



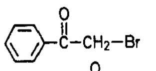
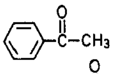
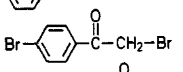
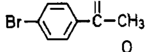
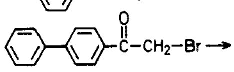
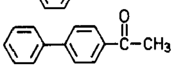
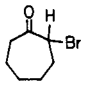
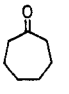
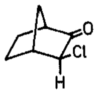
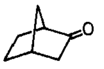
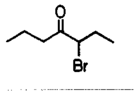
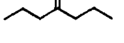
$$-\overset{O}{\overset{\|}{C}}-\underset{|}{\overset{|}{C}}-X + 2\,V^{\oplus\oplus} + H_2O \longrightarrow -\overset{O}{\overset{\|}{C}}-\underset{|}{\overset{|}{C}}-H + 2\,V^{\oplus\oplus\oplus} + X^{\ominus} + HO^{\ominus}$$

On mixing a tetrahydrofuran solution of the α-haloketone with aqueous vanadium(II) chloride, a mildly exothermic reaction takes place. After refluxing for a short period of time the halogen-free product is isolated by extractive work-up. The instantaneous complete reduction of bromoacetylarenes at room temperature shows the present method to be one of the most efficient dehalogenation procedures[6].



$$R^1-\overset{O}{\overset{\|}{C}}-\underset{X}{\underset{|}{CH}}-R^2 \xrightarrow{2\,VCl_2/H_2O/THF} R^1-\overset{O}{\overset{\|}{C}}-CH_2-R^2$$

Table. Hydrodehalogenation of α-Haloketones with Vanadium(II) Chloride in Tetrahydrofuran

α-Haloketone		Ketone	Yield[a] [%]	m.p. or b.p.[b]
	→		92	b.p. 198–200
	→		98	m.p. 48–50°
	→		96	m.p. 119–121°
	→		96	b.p. 178–180°
	→		80	
	→		88	b.p. 154–156°

[a] Yield of isolated product.

[b] The physical data found agree with literature values.

Hydrodehalogenation of α-Haloketones; General Procedure:
Solutions of the α-haloketone (5 mmol) in tetrahydrofuran (10 ml) and ~1 *M* aqueous vanadium(II) chloride (25 ml) are mixed. In the case of ω-bromoacetophenones, the mixture is immediately extracted with benzene; in all other cases, it is refluxed under nitrogen for 3–5 min and then extracted. The extract is washed with water, dried, and evaporated to provide the ketone of >98% purity (by I.R. and T.L.C. analysis), which may be further purified by distillation or recrystallization.

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