Synthetic Methods and Reactions; 79[1]. Reductive Cleavage of Oximes with Vanadium(II) Chloride

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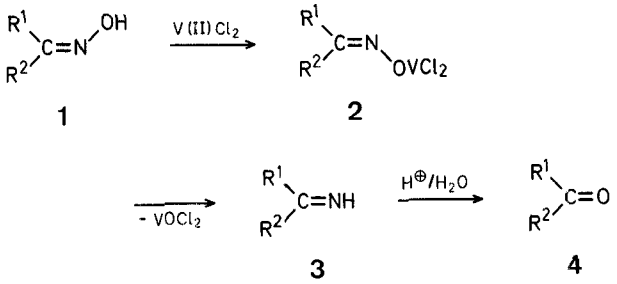
The use of transition metal ions such as titanium(II), titanium(III), chromium(II), vanadium(II), and molybdenum(III) in organic synthesis is increasing, owing to their convenient redox potentials[2]. Earlier we have demonstrated the use of a vanadium(II) reagent in hydrodehalogenation of α-haloketones[3], deoxygenation of sulfoxides[4], reduction of aryl azides[5], reductive coupling of allylic and benzilic halides[6], and reduction of benzils[7]. In continuation of studies to extend the scope of this reagent, we now report the convenient reductive deoximation of oximes **1** to carbonyl compounds **4**.



On mixing a tetrahydrofuran solution of oxime **1** with aqueous vanadium(II) chloride[8], a mildly exothermic reaction takes place. Stirring for 8 h at room temperature under nitrogen atmosphere and extractive work-up gives the pure carbonyl compounds **4** in good to excellent yields (Table). The method is complementary to those reported using molybdenum(III)[9], chromium(II)[10], and titanium(III)[11] reagents, but has the advantage of clean, high yield reactions, with ease of work-up, practically free of side products.

Reductive Cleavage of Oximes 1 with Vanadium(II) Chloride; General Procedure:

A solution of the corresponding oxime **1** (10 mmol) in tetrahydrofuran (10 ml) is rapidly added to a well-stirred solution of 1 molar aqueous vanadium(II) chloride (20 ml; prepared according to Ref. [8]) under nitrogen. The resulting mixture is stirred at room temperature for 8 h and extracted with ether (3 × 20 ml). The extract is washed twice with water (2 × 30 ml), dried with sodium sulfate, and evaporated to provide the ketone **4** of >98% purity [by I.R. and T.L.C. (silica gel) analysis]. The ketone is further purified to analytical purity by distillation or recrystallization.

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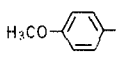
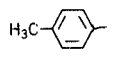
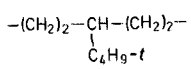
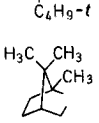
Table. Reductive Cleavage of Oximes **1** with Vanadium(II) Chloride

R^1	R^2	Yield [%][a] of **4**	m.p. or b.p./torr found	m.p. or b.p./torr reported[12]
$-(CH_2)_4-$		82	129–130 °C/760	130 °C/760
$-(CH_2)_5-$		87	40–41 °C/5.5	47 °C/15
H		91	102–103 °C/1.2	134–135 °C/12
H		88	46–47 °C/0.6	106 °C/10
		82	43–44 °C	49–50 °C
		75[b]	174–175 °C	178.8 °C
H		77	74–76 °C/20	75–78 °C/20
H_3C		93	56–57 °C/1	83–85 °C/12
H		91	56–57 °C/7	62 °C/10
H_3C	n-C_5H_{11}	92	102–103 °C/20	148–151 °C/750

[a] Yield of purified (>98%) product, checked by I.R., N.M.R., and T.L.C. (silica gel, 40:60 hexane/benzene).
[b] Reaction time 30 h.

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