

# Synthesis and Reactivity of Oxovanadium(V) Trialkoxides of Bulky and Chiral Alcohols<sup>†</sup>

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**Abstract:** The synthesis and reactivity of a series of stable oxovanadium(V) trialkoxides is reported of alcohols including *exo*-norborneol, *endo*-norborneol, 1-adamantanol, 2-adamantanol, (1*R*)-*endo*-(+)-borneol, (1*S*)-*endo*-(-)-borneol, and triphenylmethanol. The enantiomerically pure oxovanadium(V) trialkoxides, either all (+) or all (-), are significantly more stable than mixed oxovanadium(V) trialkoxides [(+, +, -) or (-, -, +)]. The reaction between VO(OR)<sub>2</sub>Cl<sub>2</sub> and alcohol to form VO(OR)<sub>2</sub>Cl and HCl was demonstrated to be reversible. The hydrolysis of the oxovanadium(V) trialkoxides was studied in organic solvents using <sup>51</sup>V NMR spectroscopy. In organic solvents a mixture of oxovanadium(V) trialkoxide and H<sub>2</sub>O is more stable than the corresponding dialkoxide hydroxide and alcohol. It appears that oxovanadium(V) trialkoxides are not inherently unstable as has been suggested by aqueous studies. The redox chemistry of oxovanadium(V) alkoxides was explored, and the derivatives were surprisingly resistant to reduction; reducing reagents such as ascorbic acid and 2-mercaptoethanol were required to reduce the vanadium(V). The unusual stability of these new oxovanadium alkoxides suggests that other derivatives with specific properties can be obtained for structural characterization or use in organic synthesis.

## Introduction

Organic oxovanadium(V) derivatives have been of recent interest to inorganic and organic chemists, as well as biochemists, spectroscopists, and material scientists, with respect to structure and reactivity.<sup>1,2</sup> The discovery of vanadium as a cofactor in bromoperoxidases<sup>3</sup> and nitrogenases<sup>4</sup> has increased the interest in the reactivity and coordination chemistry of vanadium(V) alkoxides in aqueous environments. The analogy between vanadium(V) and phosphorus, as evidenced by the structural and electronic similarities of phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) and vanadate (H<sub>2</sub>VO<sub>4</sub><sup>-</sup>, HVO<sub>4</sub><sup>2-</sup>, and VO<sub>4</sub><sup>3-</sup>), has been used in many biological studies.<sup>5-7</sup> Recent evidence in aqueous studies of enzymes accepting organic vanadates as substrates suggests an analogy between organic vanadates and organic phosphates.<sup>8,9</sup> Application of <sup>51</sup>V NMR spectroscopy to studies of the reactions of vanadate with organic ligands in aqueous solutions has led to reports of a wealth of new organic oxovanadium(V) derivatives.<sup>10-15</sup> Structural evidence, however, does suggest the oxovanadium(V) trialkoxides in the solid state prefer pentacoordinate (such as VO(OCH<sub>2</sub>CH<sub>2</sub>Cl)<sub>3</sub><sup>16</sup> and [VO(OC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O)Cl]<sub>2</sub>)<sup>17</sup> or octahedral (such as VO(OCH<sub>3</sub>)<sub>3</sub>)<sup>18</sup> environments. A vanadium-phosphorus mixed oxide of less-defined structure is the industrial catalyst that selectively oxidizes butene to maleic anhydride.<sup>19</sup> Recent applications with VOCl<sub>3</sub> and several alkoxide derivatives in organic solvents convincingly demonstrate that the unique and selective catalytic properties of vanadium oxides are not limited to heterogeneous catalysts.<sup>20-30</sup>

Oxovanadium(V) alkoxides of simple alcohols including methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol, and cyclohexanol are well-known,<sup>2,31</sup> and more complex derivatives have recently been described for diol derivatives.<sup>16</sup> In addition, other derivatives have been prepared in which one or two of the alkoxide groups have been substituted with a chlorine atom.<sup>16,17,32</sup> The tendency of these compounds to associate<sup>33</sup> and to act as Lewis acids with possible oxidation of the ligand can conveniently be utilized in synthesis and may result in formation of derivatives leading to redox reactions.<sup>30</sup>

Vanadium derivatives have been used as catalysts in selective oxidation of secondary hydroxyl functions,<sup>21</sup> in selective cleavage of ditertiary glycols,<sup>22</sup> in oxidative decarboxylation-deoxygenation of 3-hydroxycarboxylic acids,<sup>23</sup> in oxidative aromatization of  $\alpha,\beta$ -unsaturated cyclohexenones,<sup>24</sup> in oxidative deamination,<sup>25</sup> in oxidative ring opening of cyclic ketones,<sup>26</sup> in allylic oxidation,<sup>27</sup> in epoxidation of olefins,<sup>28</sup> in oxidative couplings of benzylo-

quinolines and phenethylisoquinoline synthesis,<sup>29</sup> in stereocontrolled oxidative phenolic couplings,<sup>30</sup> and in enzyme-catalyzed syntheses

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involving carbon-carbon bond formation in aldol-type reactions.<sup>9</sup> In all these reactions the presence of organic compounds leads to formation of additional oxovanadium(V) alkoxide derivatives which presumably catalyze the specific transformation. Combining catalysis of specific transformations with a chiral oxovanadium(V) derivative may be of synthetic interest in the future.

In aqueous solutions vanadate will react with ethanol on a millisecond time scale to generate ethyl vanadate and diethyl vanadate.<sup>10,15</sup> Corresponding derivatives form from *n*-propanol, isopropyl alcohol, *n*-butanol, isobutyl alcohol, *tert*-butyl alcohol, chloroethanol, and fluoroethanol.<sup>14,15</sup> The aqueous environment supports formation of the mono- and dialkoxide derivatives, and only in very concentrated alcoholic solutions are the trialkoxide oxovanadium derivatives observed.<sup>34</sup> The equilibria in aqueous solution are sensitive to pH, ionic strength, temperature, counterions, and buffers.<sup>10-15</sup> Direct comparison of the reactions in aqueous solution with those in organic solvents are therefore not commonly made. In this work we describe the preparation of stabilized vanadium(V) trialkoxide derivatives and the first successful controlled hydrolysis study in organic solvents, thus allowing a direct comparison between studies in aqueous and organic solvents.

## Experimental Section

**General Procedures. Reagents and Solvents.** The reagents used in this work were all reagent grade. Chemicals were purchased from Aldrich and dried before use unless stated otherwise. All manipulations were carried out under a nitrogen atmosphere. All solvents were dried by standard methods as described by Perrin and Armarego.<sup>35</sup>

**Spectroscopic Methods.** <sup>1</sup>H NMR spectra were recorded at 270 MHz on a Bruker-WSPY spectrometer (6.3 T). <sup>51</sup>V NMR spectra were recorded at 52.6 MHz on a Bruker-WSPY spectrometer (4.7 T). <sup>51</sup>V NMR spectra in nondeuterated solvents were recorded with external lock and chemical shifts were reported against a VOCl<sub>3</sub> reference at 0 ppm. <sup>13</sup>C NMR were recorded on a Bruker ACP-300 NMR spectrometer at 75 MHz (7.0 T) in deuterated solvents with TMS as an internal standard. IR spectra were obtained in KBr pellets on a Perkin-Elmer 1600 FT-IR spectrophotometer. Mass spectra were obtained on a VG-MM 16 spectrometer at 453 K using EI. Melting points were measured under a nitrogen atmosphere on a Fisher-Johns melting point apparatus.

**General Procedure for the Preparation of Oxovanadium(V) Trialkoxides. Oxovanadium(V) Tri-1-adamantanol (1).** The oxovanadium(V) alkoxides were prepared by using similar procedures where only solvents, specific scale of reaction, and characterization of the compounds differ. The preparation of oxovanadium(V) tri-1-adamantanol therefore serves as a general example and the differences are indicated for each compound. A clear and colorless solution of 1-adamantanol (0.46 g, 3.0 mmol) was stirred in 50 mL of toluene at ambient temperature in a 100-mL two-neck round-bottom flask. A solution of VOCl<sub>3</sub> (1.0 mmol, 0.094 mL) in toluene (10 mL) was added dropwise with a syringe to the flask over a period of 5 min. When all the VOCl<sub>3</sub> was added, the solution went from red to golden, and eventually a white fog of HCl formed above the solution. After it was stirred for 10 h at ambient temperature, the solution was yellow with no further HCl gas evolution. At that point, ammonia was bubbled through the solution for 5 min at a rate of 100

mL/min and the solution turned colorless while a white precipitate of ammonium chloride formed. The precipitate was removed by filtration and the filtrate was kept at 253 K up to one week under a nitrogen atmosphere until the solid product precipitated. The resulting 0.31 g (0.60 mmol) of oxovanadium(V) tri-1-adamantoxide corresponds to a yield of 60%.

**Specific Procedures. Synthesis. Oxovanadium(V) Tri-*exo*-norborneol (2).** The reaction was performed by using 0.34 g (3.0 mmol) *exo*-norborneol in hexanes. The yield was 0.22 g (0.55 mmol), corresponding to a reaction yield of 55%. The product was characterized as follows: mp 63–64 °C. <sup>51</sup>V NMR (hexanes): δ –620 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.03 (1 H, d), 2.45 (1 H, d), 2.25 (1 H, s), 1.82 (1 H, q), 1.49 (4 H, m), 1.10 (3 H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 93.1, 45.1, 43.6, 35.3, 34.6, 28.3, 24.3. IR (KBr):  $\nu_{\text{V=O}} = 998.6 \text{ cm}^{-1}$  (s). Mass spectrum: *m/e* 400 (M<sup>+</sup>), 288 (M<sup>+</sup> – C<sub>7</sub>H<sub>11</sub>OH), 212 (M<sup>+</sup> – 2C<sub>7</sub>H<sub>10</sub>), 194 (M<sup>+</sup> – C<sub>7</sub>H<sub>11</sub>OH – C<sub>7</sub>H<sub>10</sub>), 112 (C<sub>7</sub>H<sub>11</sub>OH), 94 (C<sub>7</sub>H<sub>10</sub>). Elemental analysis: % C 62.78 (calcd 62.99), % H 8.26 (calcd 8.31), % V 12.79 (calcd 12.72).

**Oxovanadium(V) Tri-*endo*-norborneol (3).** The reaction was carried out using 0.34 g (3.0 mmol) of *endo*-norborneol in hexanes. The yield was 0.24 g (0.60 mmol), corresponding to 60%. The product was characterized as follows: mp 58–60 °C. <sup>51</sup>V NMR (hexanes): δ –596 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.60 (1 H, s), 2.53 (1 H, s), 2.15 (2 H, m), 1.85 (1 H, m), 1.55 (1 H, m), 1.35 (4 H, m), 0.90 (1 H, q). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 91.9, 44.1, 40.5, 37.4, 29.7, 20.3. IR (KBr):  $\nu_{\text{V=O}} = 1004 \text{ cm}^{-1}$  (s). Mass spectrum: *m/e* 400 (M<sup>+</sup>), 306 (M<sup>+</sup> – C<sub>7</sub>H<sub>10</sub>), 288 (M<sup>+</sup> – C<sub>7</sub>H<sub>11</sub>OH), 212 (M<sup>+</sup> – 2C<sub>7</sub>H<sub>10</sub>), 194 (M<sup>+</sup> – C<sub>7</sub>H<sub>11</sub>OH – C<sub>7</sub>H<sub>10</sub>), 112 (C<sub>7</sub>H<sub>11</sub>OH), 94 (C<sub>7</sub>H<sub>10</sub>). Elemental analysis: % C 63.21 (calcd 62.99), % H 8.37 (calcd 8.31), % V 12.65 (calcd 12.72).

**Oxovanadium(V) Tri-1-adamantanol (1).** The yield was 60% in a reaction with 0.46 g (3.0 mmol) of 1-adamantanol in toluene (see above). The product was characterized as follows: Sublimes at 156 °C. <sup>51</sup>V NMR (toluene): δ –661 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.18 (3 H, s), 1.92 (6 H, d), 1.62 (6 H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 83.5, 45.4, 36.1, 31.4. IR (KBr):  $\nu_{\text{V=O}} = 999.4$  (s),  $952 \text{ cm}^{-1}$  (m),  $\nu_{\text{C-H}} = 642 \text{ cm}^{-1}$  (w). Mass spectrum: *m/e* 520 (M<sup>+</sup>), 465 (M<sup>+</sup> – C<sub>4</sub>H<sub>7</sub>), 426 (M<sup>+</sup> – C<sub>7</sub>H<sub>10</sub>), 368 (M<sup>+</sup> – C<sub>10</sub>H<sub>15</sub>OH), 218 (M<sup>+</sup> – 2C<sub>10</sub>H<sub>15</sub>O), 152 (C<sub>10</sub>H<sub>15</sub>OH), 135 (C<sub>10</sub>H<sub>15</sub>), 94 (C<sub>7</sub>H<sub>10</sub>). Elemental analysis: % C 68.97 (calcd 69.21), % H 8.63 (calcd 8.71), % V 9.83 (calcd 9.78).

**Oxovanadium(V) Tri-2-adamantanol (4).** The reaction was carried out using 0.46 g (3.0 mmol) of 2-adamantanol in toluene, and the yield was 0.32 g (0.62 mmol), corresponding to 62% yield. The product was characterized as follows: Decomposition at 200 °C. <sup>51</sup>V NMR (toluene): δ –610 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.26 (1 H, s), 2.19 (2 H, s), 2.04 (2 H, d), 1.80 (8 H, m), 1.45 (2 H, d). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 93.9, 37.5, 36.6, 35.9, 31.3, 27.5, 27.0. IR (KBr):  $\nu_{\text{V=O}} = 1000 \text{ cm}^{-1}$  (s),  $\nu_{\text{C-H}} = 629 \text{ cm}^{-1}$  (w). Mass spectrum: *m/e* 520 (M<sup>+</sup>), 368 (M<sup>+</sup> – C<sub>10</sub>H<sub>15</sub>OH), 331 (M<sup>+</sup> – C<sub>10</sub>H<sub>14</sub> – C<sub>4</sub>H<sub>7</sub>), 234 (M<sup>+</sup> – C<sub>10</sub>H<sub>15</sub>OH – C<sub>10</sub>H<sub>14</sub>), 152 (C<sub>10</sub>H<sub>15</sub>OH), 134 (C<sub>10</sub>H<sub>14</sub>), 84 (C<sub>6</sub>H<sub>12</sub>). Elemental analysis: % C 69.45 (calcd 69.21), % H 8.77 (calcd 8.71), % V 9.73 (calcd 9.78).

**Oxovanadium(V) Tri-(1*S*)-*endo*-(-)-borneol (5).** The reaction was performed with 0.46 g (3.0 mmol) of (1*S*)-*endo*-(-)-borneol in hexanes. The specific rotation of the starting alcohol was  $[\alpha]_{25}^{c} -37.1^{\circ}$ , when *c* = 0.50 in hexanes. The enantiomeric purity of the alcohol was determined by using Eu(thf)<sub>3</sub> in CDCl<sub>3</sub> and no detectable *R* isomer was observed; we saw distinctive <sup>1</sup>H NMR resonances in these solutions when 1% and 2% *R* enantiomers were added, leading to the conclusion that the starting material had an ee higher than 98%. The yield was 0.29 g (0.55 mmol), corresponding to a yield of 55%. The product was characterized as follows: mp 138–140 °C. Specific rotation  $[\alpha]_{25}^{c} = -29.5^{\circ}$  when *c* = 0.50 (hexanes). <sup>51</sup>V NMR (hexanes): δ –598 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.43 (1 H, d), 2.45 (1 H, m), 1.85 (1 H, m), 1.65 (2 H, m), 1.22 (2 H, m), 0.90 (10 H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 97.5, 52.3, 48.2, 45.4, 40.0, 28.2, 26.3, 20.2, 18.9, 13.7. IR (KBr):  $\nu_{\text{V=O}} = 1004.0 \text{ cm}^{-1}$  (s),  $\nu_{\text{C-H}} = 646.4 \text{ cm}^{-1}$  (w). Mass spectrum: *m/e* 526 (M<sup>+</sup>), 372 (M<sup>+</sup> – C<sub>10</sub>H<sub>17</sub>OH), 236 (M<sup>+</sup> – C<sub>10</sub>H<sub>17</sub>OH – C<sub>10</sub>H<sub>16</sub>), 154 (C<sub>10</sub>H<sub>17</sub>OH), 136 (C<sub>10</sub>H<sub>16</sub>).

**Oxovanadium(V) Tri-(1*R*)-*endo*-(+)-borneol (6).** The reaction was performed with 0.46 g (3.0 mmol) of (1*R*)-*endo*-(+)-borneol in hexanes. The specific rotation of the alcohol was  $[\alpha]_{25}^{c} +30.8^{\circ}$ , when *c* = 0.50 in hexanes. The enantiomeric purity of the alcohol was determined by <sup>1</sup>H NMR using Eu(thf)<sub>3</sub> in CDCl<sub>3</sub> and was found to contain 5% of the *S* enantiomer resulting in an ee of 90%. The yield was 0.29 g (0.55 mmol), corresponding to a yield of 55%. The product was characterized as follows: mp 130–132 °C. Specific rotation  $[\alpha]_{25}^{c} = +26.4^{\circ}$  when *c* = 0.25,  $+26.6^{\circ}$  when *c* = 0.50, and  $+27.0^{\circ}$  when *c* = 1.0. <sup>51</sup>V NMR (hexanes): δ –598 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.44 (1 H, d), 2.45 (1 H, m), 1.85 (1 H, m), 1.66 (2 H, m), 1.23 (2 H, m), 0.90 (10 H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 97.3, 51.8, 48.1, 45.2, 39.9, 28.1, 26.2, 20.1, 18.8, 13.6. IR (KBr):  $\nu_{\text{V=O}} = 1003.3 \text{ cm}^{-1}$  (s),  $\nu_{\text{C-H}} = 645.9 \text{ cm}^{-1}$  (w). Mass spectrum: *m/e* 526 (M<sup>+</sup>), 372 (M<sup>+</sup> – C<sub>10</sub>H<sub>17</sub>OH), 236 (M<sup>+</sup> – C<sub>10</sub>H<sub>17</sub>OH)

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– C<sub>10</sub>H<sub>16</sub>), 154 (C<sub>10</sub>H<sub>17</sub>OH), 136 (C<sub>10</sub>H<sub>16</sub>). Elemental analysis: % C 68.61 (calcd 68.41), % H 9.79 (calcd 9.76), % V 9.63 (calcd 9.67).

**Oxovanadium(V) Tris(triphenylmethanol) (7).** A yellow solution of VO(OCH<sub>3</sub>)<sub>3</sub> (0.250 g, 1.56 mmol) in 50 mL of toluene was prepared in a 100-mL two-neck round-bottom flask under nitrogen. Solid triphenylmethanol (1.22 g, 4.69 mmol) was added directly to the solution and the mixture was stirred at ambient temperature. A condenser was connected to the flask and the solution was refluxed for 20 min. A cloudy yellowish solution with a yellow-green precipitate formed. The heating was stopped, and the solvent was removed in vacuo at ambient temperature. The yellow product was redissolved in toluene and the undesired decomposition product removed by vacuum filtration. Analysis of the crude reaction product by <sup>1</sup>H NMR revealed that the product contained about 20% unreacted ligand. The <sup>51</sup>V NMR spectrum showed that the solution was comprised of two products. The major product at –733 ppm contained 60% of the vanadium present and the minor product at –706 ppm contained the remaining 40%. After recrystallizing the solid in toluene, the resulting product was white and the <sup>51</sup>V NMR spectrum showed only the –733 ppm product. Four recrystallizations in toluene were necessary to remove all the unreacted ligand. The resulting purified product weighed 0.179 g (0.331 mmol), which corresponds to an overall yield of 21%. The product was characterized as follows: mp 195–197 °C. <sup>51</sup>V NMR (CDCl<sub>3</sub>): δ –733 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.10 ppm (45 H, m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 146.6, 128.9, 127.9, 127.5 ppm. IR (KBr): ν<sub>V=O</sub> = 980.0 cm<sup>–1</sup> (vs), ν<sub>V–O</sub> = 636.1 cm<sup>–1</sup> (s). Elemental analysis: % C 80.77 (calcd 81.03), % H 5.42 (calcd 5.37), % V 6.13 (calcd 6.03).

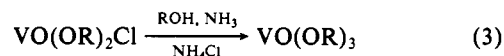
**Specific Spectroscopic Studies. Equilibrium Reactions between VO(O-1-Ad)<sub>3</sub> (1) and HCl.** A solution containing 100 mM VO(O-1-Ad)<sub>2</sub>Cl was generated by dissolving 0.0500 mmol (0.0260 g) of VO(O-1-Ad)<sub>3</sub> (1) in 0.50 mL of CHCl<sub>3</sub> in a 5-mm NMR tube capped with a rubber septum and injecting 1.50 mL of HCl gas into the NMR tube followed by shaking of the solution. A <sup>51</sup>V NMR spectrum of the solution was recorded 30 min later and showed only the presence of VO(O-1-Ad)<sub>2</sub>Cl (–520 ppm). In order to remove excess HCl, nitrogen was bubbled through the solution for 1 h. Using a 2.00-mL syringe, HCl gas was then continuously added under the solvent surface of the 2.0-mL NMR tube containing 0.5 mL of 100 mM VO(O-1-Ad)<sub>2</sub>Cl. After each addition, the tube was shaken and the <sup>51</sup>V NMR spectrum recorded 30 min later. The reaction equilibrium established quite rapidly and no changes were observed as a function of time. In any event, the solutions were thoroughly shaken after the HCl addition, and the NMR was recorded 30 min later in order to ascertain that the equilibrium between HCl in the gas phase and liquid was established. A maximum of 1.20 mL of HCl gas was added; at no time did the NMR tubes exhibit signs of pressure buildup.

**Hydrolysis Studies of VO(O-1-Ad)<sub>3</sub> (1) in CHCl<sub>3</sub>.** Three stock solutions were prepared in order to generate a series of solutions containing various concentrations of total oxovanadium(V) compounds and water in CHCl<sub>3</sub>. A stock solution of 1 contained 40 mM trialkoxide in CHCl<sub>3</sub>, and a second stock solution contained 10 mM H<sub>2</sub>O in CHCl<sub>3</sub> (0.090 g of H<sub>2</sub>O in 500 mL of dry CHCl<sub>3</sub>). A third stock solution was dry CHCl<sub>3</sub> that was added to obtain the desired final concentrations of oxovanadium trialkoxide and H<sub>2</sub>O. A calculated volume of 1 was added first to the 5-mm NMR tube, followed by addition of the H<sub>2</sub>O solution. The dry CHCl<sub>3</sub> was added last so that the appropriate concentrations of 1 and H<sub>2</sub>O were obtained (35–13 mM oxovanadium(V) trialkoxide and 5–8.3 mM H<sub>2</sub>O). The solutions were mixed thoroughly, and after 30 min <sup>51</sup>V NMR spectra were recorded.

A solution of partially hydrolyzed 1 was evaporated to dryness and a mass spectrum of the mixture was recorded. The spectrum contained both the molecular ions for 1 and the oxovanadium(V) hydroxo di-1-adamantoxide (*m/e* 386 (M<sup>+</sup>)). The latter ion is not observed in a mass spectrum (EI) of pure 1 and is therefore attributed to the hydrolysis product.

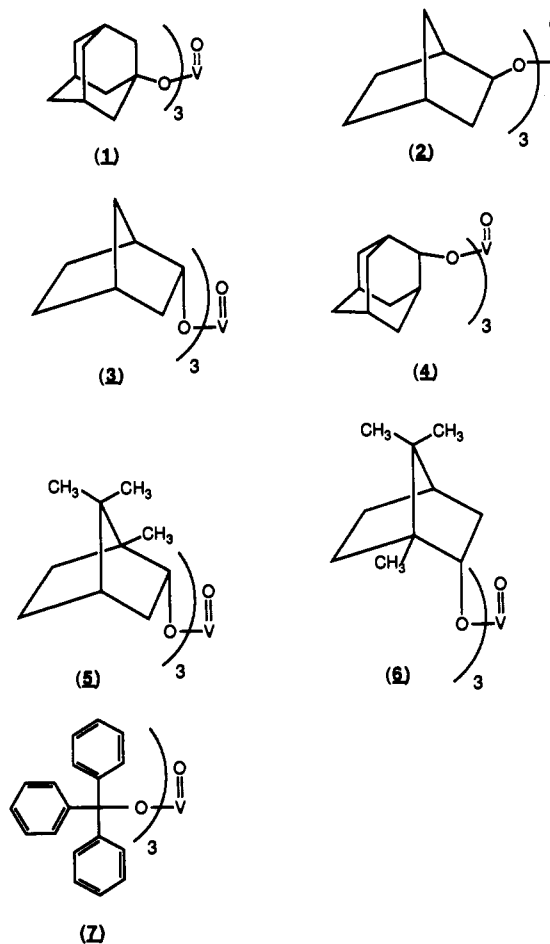
## Results and Discussion

**Synthesis of New Oxovanadium(V) Trialkoxides.** A series of new oxovanadium(V) trialkoxides were prepared from VOCl<sub>3</sub> and alcohol at 25 °C as shown in reactions 1–3. The reaction of



VOCl<sub>3</sub> with 3 equiv of 1-adamantanol is discussed here as a representative case for compounds 1–6. A few minutes after

Chart I

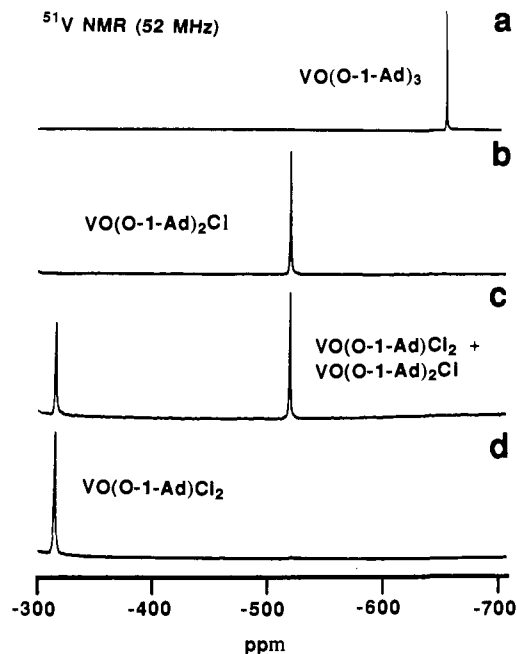


VOCl<sub>3</sub> and 1-Ad-OH were combined in CHCl<sub>3</sub> the <sup>51</sup>V NMR resonance at 0 ppm for VOCl<sub>3</sub> was joined by a second signal at –318 ppm assigned to VO(O-1-Ad)Cl<sub>2</sub>. Within 30 min a resonance appeared at –518 ppm, which was assigned to VO(O-1-Ad)<sub>2</sub>Cl. In order to remove the last chlorine atom, it was necessary to bubble NH<sub>3</sub> through the solution. In general, the amount of reduction products was minimized by assuring that all of the HCl was removed, for example, by bubbling N<sub>2</sub> through the solution before the NH<sub>3</sub> was added. We routinely stirred the solutions for 10 h before adding NH<sub>3</sub>. Similar results could be obtained in 4–5 h if N<sub>2</sub> was bubbled through the solution.

Compounds 1–6 could also be prepared by the transesterification method, but we did not include experimental details for these systems. Compound 7, however, was not prepared through reactions 1–3 since extensive reduction occurred when this route was attempted. This material was prepared by transesterification of VO(OCH<sub>3</sub>)<sub>3</sub> with triphenylmethanol in toluene. Smaller amounts of reduction products were observed in this reaction although several recrystallizations were necessary to remove excess ligand and obtain the material in pure form.

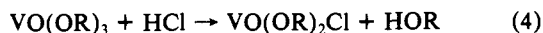
The alcohols described in this work were generally selected for their bulkiness, so that the resulting alkoxides would be monomeric and lead to compounds containing tetrahedral vanadium(V). The *R-endo*-borneol and *S-endo*-borneol ligands were chosen so that the resulting oxovanadium(V) trialkoxide products were chiral.

**Reversibility of Reactions.** Although reactions 1–3 were first described at the turn of the century,<sup>30d</sup> the question of their reversibility has not been explored. In view of the recent application of several of these materials in organic synthesis,<sup>22–29</sup> it is of interest to explore the stability and reactivity of these compounds. It is well-known that to prepare both mono- and dichlorooxovanadium(V) alkoxides from the trialkoxides one can use acetyl chloride.<sup>2</sup> It is possible that the reaction of oxovanadium(V) trialkoxide with acetyl chloride could be mimicked by HCl. The fact that NH<sub>3</sub> is required (with resulting precipi-



**Figure 1.**  $^{51}\text{V}$  NMR spectra (52 MHz) monitor the reaction of  $\text{VO}(\text{O}-1\text{-Ad})_3$  with HCl at time (a) 0 s ( $\text{VO}(\text{O}-1\text{-Ad})_3$ ), (b) 30 s ( $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$ ), (c) 60 s ( $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl} + \text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2$ ), and (d) 2 min ( $\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2$ ).

tation of  $\text{NH}_4\text{Cl}$ ) when replacing the last chlorine in  $\text{VOCl}_3$  suggests that the reaction of oxovanadium(V) dialkoxo chloride with alcohol in the presence of HCl may be reversible. We therefore set out to explore the reversibility of reaction 4.



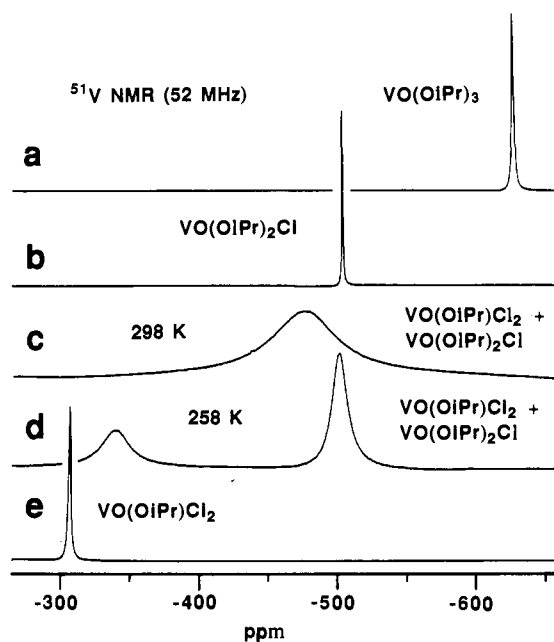
After HCl is bubbled through a chloroform solution of oxovanadium(V) tri-1-adamantoxide ( $-658$  ppm, Figure 1a) for 30 s, the resulting  $^{51}\text{V}$  NMR spectrum showed one signal at  $-522$  ppm (see Figure 1b). All the oxovanadium(V) trialkoxide at  $-658$  ppm had reacted with HCl to generate the monochloride. If HCl was bubbled through the solution for a total of 60 s, both the oxovanadium(V) di-1-adamantoxo chloride ( $-522$  ppm) and the oxovanadium(V)-1-adamantoxo dichloride ( $-318$  ppm) are observed in the  $^{51}\text{V}$  NMR spectrum (Figure 1c). Bubbling HCl through the solution for 2 min gave rise to complete conversion to the oxovanadium(V) 1-adamantoxo dichloride (Figure 1d). Additional treatment of the dichloride for a prolonged time (up to 4 h) with HCl at ambient temperatures did not produce any evidence for  $\text{VOCl}_3$ . These observations demonstrate that both reactions (2) and (4) are reversible.

The position of the equilibrium of reaction 2 was also explored. The oxovanadium(V) tri-1-adamantoxide was dissolved in  $\text{CHCl}_3$  and HCl was pumped through the solution until all the oxovanadium(V) trialkoxide was converted to  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$ . Then  $\text{N}_2$  was bubbled through the stock solution of  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$  to remove excess HCl (about 30 min). Addition of 0–1.20 mL of HCl gas to solutions of  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$  treated in the above manner will shift the position of the equilibrium of reaction 2 in respective solutions. The HCl distributes itself in both the solution and the volume of gas above the solution. The moles of added free HCl in the liquid ( $n_{\text{liq}}$ ) were calculated from the total moles of free HCl ( $n_{\text{tot/free}}$ ) and the solubility of HCl in  $\text{CHCl}_3$ . Since the total moles of free HCl are defined as shown by (5), the moles of free HCl in the gas above the liquid can be calculated ( $n_{\text{gas}}$ ). We can combine Henry's law,  $P_1 = K(n_{\text{liq}}/n_{\text{solvent}})$ , where  $K$  is the HCl solubility constant in  $\text{CHCl}_3$ ,  $n_{\text{solvent}}$  is the moles of solvent, and  $P_1$  is the partial pressure of the free HCl distributed in the liquid phase, with the relationship  $P_1V = n_{\text{gas}}RT$ , which results in eq 6. The free HCl in the liquid and gas phases is calculated as shown in (7). In the present case where HCl is dissolved in  $\text{CHCl}_3$  and a 1.5-mL volume of gas is above the solution in the

**Table I.** Concentrations of  $[\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}]$ ,  $[\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2]$ ,  $[\text{HO}-1\text{-Ad}]$ , and  $[\text{HCl}]$  after Adding Various Amounts of HCl to a Solution of 100 mM  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$

HCl added, vol/mol	$[\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}]$ , <sup>a</sup> mM	$[\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2]$ , <sup>a</sup> mM	$[\text{ROH}]$ , mM	$[\text{HCl}]_{\text{free,liq}}$ , mM
0.20/0.0068	86.8	13.2	113	0.278
0.40/0.0136	74.8	25.2	125	1.39
0.70/0.0238	56.1	43.9	144	2.50
0.90/0.0306	45.5	54.5	154	4.65
1.20/0.0408	33.7	66.3	166	10.60

<sup>a</sup> These concentrations were measured by recording  $^{51}\text{V}$  NMR spectra of solutions containing 100 mM of total vanadium. The parameters for recording the 52-MHz  $^{51}\text{V}$  NMR spectra were a sweep width of 16000 Hz, a pulse width of 90°, an accumulation time of 0.13 s, no relaxation delay, and ambient temperature.



**Figure 2.**  $^{51}\text{V}$  NMR spectra (52 MHz) show (a)  $\text{VO}(\text{OiPr})_3$ , (b)  $\text{VO}(\text{OiPr})_2\text{Cl}$ , (c)  $\text{VO}(\text{OiPr})_2\text{Cl} + \text{VO}(\text{OiPr})\text{Cl}_2$  at 298 K, (d) same as (c) at 258 K, and (e)  $\text{VO}(\text{OiPr})\text{Cl}_2$ .

NMR tube, the  $n_{\text{liq}}/n_{\text{tot}} = 0.69$ , suggesting 69% of all free HCl is dissolved in  $\text{CHCl}_3$ . The equilibrium constant of reaction 2

$$n_{\text{tot/free}} = n_{\text{gas}} + n_{\text{liq}} \quad (5)$$

$$\frac{n_{\text{liq}}}{n_{\text{tot/free}}} = \frac{1}{1 + \frac{KV}{RTn_{\text{solvent}}}} \quad (6)$$

$$[\text{HCl}]_{\text{total}} = [\text{HCl}]_{\text{free,gas}} + [\text{HCl}]_{\text{free,liq}} + [\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2] \quad (7)$$

( $K_{(2)}$ ) is defined as shown in (8).

$$K_{(2)} = \frac{[\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}][\text{HCl}]}{[\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2][\text{ROH}]} \quad (8)$$

The concentrations of  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$  and  $\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2$  in solutions in which known total amounts of HCl have been added to known concentrations of the monochloride in  $\text{CHCl}_3$  are shown in Table I. Using the data in Table I and (8), the equilibrium constant  $K_{(2)}$  was calculated and found to be 0.03 ( $\pm 0.01$ ). The low  $K_{(2)}$  suggests that  $\text{VO}(\text{O}-1\text{-Ad})\text{Cl}_2$  is significantly more stable in the presence of HCl and HO-1-Ad than  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$ . These findings imply that the synthesis of  $\text{VO}(\text{O}-1\text{-Ad})_2\text{Cl}$  (and  $\text{VO}(\text{O}-1\text{-Ad})_3$ ) proceeds because HCl is removed from the reaction flask during the reaction.

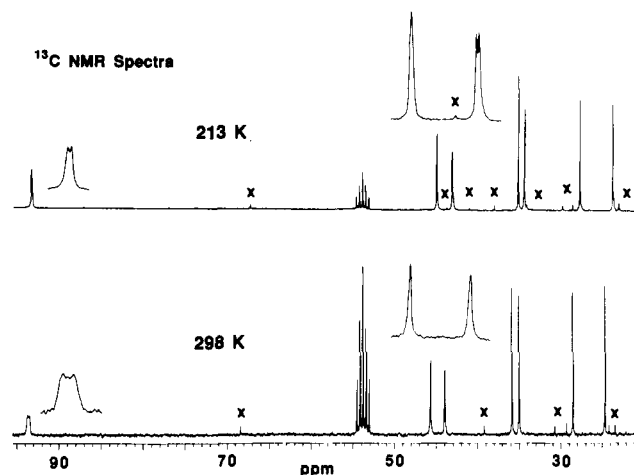
To demonstrate that the reversibility observed with the adamantane compounds also exists with other well-characterized trialkoxides, we examined the reversibility in the reactions of

oxovanadium(V) triisopropoxide with HCl (Figure 2). HCl was added to a 3.0-mL solution of 300 mM oxovanadium(V) triisopropoxide in pentane ( $-630$  ppm) (Figure 2a) at ambient temperature by pumping HCl through the solution for 12 s. This solution contained only the monochloride ( $-502$  ppm) (Figure 2b). If HCl was pumped through the solution for 20 s, a broad signal at about  $-480$  ppm was observed (Figure 2c). If the HCl was added for 30 s, a sharp signal at  $-307$  ppm was observed, corresponding to the oxovanadium(V) isopropoxy dichloride ( $\text{VO}(\text{OiPr})\text{Cl}_2$ ) (Figure 2e). The broad signal at  $-480$  ppm is most likely due to a mixture of  $\text{VO}(\text{OiPr})_2\text{Cl}$  and  $\text{VO}(\text{OiPr})\text{Cl}_2$  rapidly exchanging at 298 K. A spectrum of this solution shown in Figure 2d was recorded at 258 K and indeed shows that the broad signal is frozen out into two signals: a broader signal for the  $\text{VO}(\text{OiPr})_2\text{Cl}$  ( $-502$  ppm) and another broad signal attributed to the  $\text{VO}(\text{OiPr})\text{Cl}_2$ . It is possible that the "free" HCl in solution is interacting with both these compounds since similar exchange does not occur in solutions without HCl.<sup>20</sup> It is interesting to note that the exchange reaction between the vanadium complexes of isopropyl alcohol (the less steric alcohol) is much faster than the exchange rate between the vanadium complexes of 1-adamantanol (the more steric alcohol).

The reaction of  $\text{VO}(\text{OR})_3$  with HCl occurs very cleanly, and HCl can therefore be substituted for acetyl chloride in the preparation of chlorides from  $\text{VO}(\text{OR})_3$ . In fact it may be the presence of HCl in such solutions that promotes the reaction. As shown in Figure 2b, the reaction can be stopped at the monochloride. However, further treatment of  $\text{VO}(\text{OR})_2\text{Cl}$  with HCl will favor the formation of  $\text{VO}(\text{OR})\text{Cl}_2$  since  $\text{VO}(\text{OR})\text{Cl}_2$  is more stable in the presence of HCl. In summary, reactions 2 and 4 are reversible reactions, and in the presence of free HCl the equilibrium favors  $\text{VO}(\text{OR})\text{Cl}_2$ . The faster reaction times of  $\text{VO}(\text{OR})\text{Cl}_2$  compounds compared to  $\text{VO}(\text{OR})_3$  as catalysts in oxidation of organic compounds in alcoholic solvents<sup>26,28</sup> may reflect the inherent content of HCl in the reaction. These findings suggest that  $\text{VO}(\text{OR})_3$ ,  $\text{VO}(\text{OR})_2\text{Cl}$ , and  $\text{VO}(\text{OR})\text{Cl}_2$  should have the same catalytic effects in synthetic applications if appropriate amounts of HCl were added.

**Structural Characterization in Solution.** Oxovanadium(V) alkoxides of alcohols including methanol, ethanol, and isopropyl alcohol are known to associate extensively in solution. It was previously shown that the  $^{51}\text{V}$  NMR chemical shifts of such vanadium alkoxides increase as the concentration of the compound increases.<sup>33</sup> The chemical shift for oxovanadium(V) trimethoxide changes more than 40 ppm when the concentration increases from 1 mM to more than 500 mM. The  $^{51}\text{V}$  chemical shift did not vary in toluene, chloroform, and hexanes solutions from 1.0 to 500 mM for oxovanadium(V) tri-1-adamantanol, oxovanadium(V) tri-endo-borneol, and oxovanadium(V) tri-*exo*-norborneol. The bulky alcohols introduced in these studies are therefore less likely to favor association around the small vanadium atom.

The  $^1\text{H}$  NMR chemical shifts for the protons on the carbon adjacent to the alcohol moiety shift from 1.3 to 1.5 ppm upon vanadylation. More distant protons show a shift ranging from 0 to 0.4 ppm. The  $^{13}\text{C}$  NMR spectra show the carbon  $\alpha$  to the oxygen shifts from 19 to 25 ppm downfield. All the other carbons shift very little and less than 2 ppm. The broadening of the signal for the  $\alpha$ -carbon suggested the possibility that some exchange processes may occur at ambient temperature. In the case of the  $^{13}\text{C}$  NMR spectrum of oxovanadium(V) tri-*exo*-norborneol, lowering the temperature to 213 K gave a doublet for the  $\alpha$ -carbon and a doublet for the bridgehead carbon (see Figure 3). The  $^{13}\text{C}$  NMR spectrum at 213 K thus suggests the presence of two types of carbon attached to a vanadium atom, although no evidence is seen of chemical exchange. Previously, Raman, IR, and NMR spectroscopy were used to examine the conformational populations for  $C_{3v}$  and  $C_s$  derivatives of oxovanadium(V) tri-*tert*-butoxide.<sup>36</sup> The  $C_{3v}$  conformation of  $\text{VO}(\text{OCH}_2\text{CH}_2\text{Cl})_3$  has recently been found by X-ray crystallography, suggesting that the  $C_{3v}$  structure



**Figure 3.** Proton-decoupled  $^{13}\text{C}$  NMR spectra (at 75 MHz) were recorded at 298 and 213 K of 350 mM oxovanadium(V) tri-*exo*-norborneol. The  $\alpha$ -carbon atom signal is indicated and the scale expanded to show the coupling pattern and width of resonance. The parameters used were a pulse width of  $30^\circ$ , a relaxation delay of 1.05, an accumulation time of 0.81 s, a sweep width of 20 000 Hz, and a decoupling power of 16 T. Impurities in the reaction mixture and solvent resonances are marked by X; the impurities can be removed by crystallization.

is more favorable in the solid state.<sup>16</sup> The  $C_{3v}$  and the  $C_s$  structures of oxovanadium(V) tri-*tert*-butoxide were assigned to  $^{13}\text{C}$  NMR chemical shifts in the solid state and solution at both ambient and elevated temperatures.<sup>36</sup> Analogous  $^{13}\text{C}$  chemical shift changes were not observed with compounds 1–7. Since compounds 1–4 are more sterically demanding than oxovanadium tri-*tert*-butoxide, one would have expected both the  $C_{3v}$  and the  $C_s$  forms, in accord with previous findings. We therefore reexamined the  $^{13}\text{C}$  NMR studies of  $\text{VO}(\text{O}-t\text{-Bu})_3$  reported previously.

A solution of colorless  $\text{VO}(\text{O}-t\text{-Bu})_3$  that by  $^{51}\text{V}$  NMR has one signal at  $-673$  ppm is found to contain only one resonance in the  $^{13}\text{C}$  NMR spectrum in the  $\alpha$ -carbon region (83.9 ppm). Previously, a second signal at 86.9 ppm was also observed and attributed to the second rotational isomer of the  $\text{VO}(\text{O}-t\text{-OBu})_3$ . As we will show below, the addition of 1 equiv of  $\text{H}_2\text{O}$  to a  $\text{VO}(\text{O}-t\text{-OBu})_3$  sample will generate a mixture containing the hydrolysis product presumed to be  $\text{VO}(\text{O}-t\text{-OBu})_2\text{OH}$  and  $\text{VO}(\text{O}-t\text{-Bu})_3$ , which by  $^{51}\text{V}$  NMR show two signals at  $-659$  and  $-673$  ppm. This mixture gives a  $^{13}\text{C}$  NMR spectrum that contains two resonances in the region of interest; 86.9 and 83.9 ppm. These two signals in the  $^{13}\text{C}$  NMR spectrum are signals for the  $\alpha$ -carbons of the trialkoxide and its hydrolysis product; dry unhydrolyzed  $\text{VO}(\text{O}-t\text{-Bu})_3$  does not contain a signal at 86.9 ppm. As seen in Figure 3, low-temperature NMR spectra show that the solution contains two types of  $\alpha$ -carbons and two C1 carbons at equal intensity. At ambient temperature in  $\text{CD}_2\text{Cl}_2$  (Figure 3) and elevated temperatures up to 373 K in  $\text{CDCl}_3$  (data not shown), the spectra show no evidence for exchange; the two signals for the  $\alpha$ -carbon and the C1's merge as a result of the temperature effects on chemical shift. If indeed exchange occurred between the  $C_{3v}$  and  $C_s$  rotational isomers, one would anticipate changes in populational isomers over the 160-deg temperature range we examined. We therefore conclude that the two rotational isomers cannot be observed by magnetic resonance for oxovanadium(V) trialkoxy systems and that either just one form is present in solution or they exchange too rapidly to be observed by low-temperature NMR spectroscopy in the temperature range we examined.

Carbons in close proximity to the vanadium in compounds 1–3 exhibit a pattern of wide lines at high/ambient temperature and sharp lines at low temperature. These changes in line widths for the  $\alpha$ -carbon are due to changes in relaxation times for the vanadium. Since vanadium is a quadrupole, the relaxation time of vanadium is very sensitive to viscosity. At low temperatures the relaxation times for the vanadium are very short and, as a consequence, eliminate the vanadium-carbon coupling that was almost visible at ambient temperatures. We tested this possibility by

(36) Witke, K.; Lachowitz, A.; Bruser, W.; Zeigan, D. Z. *Anorg. Allg. Chem.* 1980, 465, 193–203.

**Table II.** Hydrolysis of Oxovanadium(V) Tri-1-adamantoxide (VO(O-1-Ad)<sub>3</sub>) in CHCl<sub>3</sub><sup>a</sup>

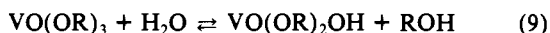
concn of total H <sub>2</sub> O, mM	concn of total vanadium, mM	nature of solutn	concn of VO(O-1-Ad) <sub>3</sub> , <sup>b</sup> mM	concn of VO(O-1-Ad) <sub>2</sub> OH, <sup>c</sup> mM	concn of free H <sub>2</sub> O, mM	concn of free adamantanol	K <sub>hyd</sub>
5.5	35.6	clear, colorless	31.0	4.5	1.0	4.5	0.6
6.6	26.7	clear, light yellow	22.2	4.5	2.1	4.5	0.4
7.5	20.0	clear, light yellow	15.0	4.9	2.5	4.9	0.6
8.0	16.0	clear, light yellow	11.4	4.6	3.4	4.6	0.5
8.3	13.3	clear, light yellow	9.2	4.1	4.3	4.1	0.4

<sup>a</sup>The concentrations of VO(O-1-Ad)<sub>3</sub> (-658 ppm) and VO(O-1-Ad)<sub>2</sub>OH (-646 ppm) were calculated from the known total vanadium concentration and the integrations of the <sup>51</sup>V NMR resonances. The parameters for recording the 79-MHz <sup>51</sup>V NMR spectra were a sweep width of 29 000 Hz, a pulse width of 45°, an accumulation time of 0.10 s, no relaxation delay, and ambient temperature. <sup>b</sup>δ <sup>51</sup>V: -658 ppm. <sup>c</sup>δ <sup>51</sup>V: -646 ppm.

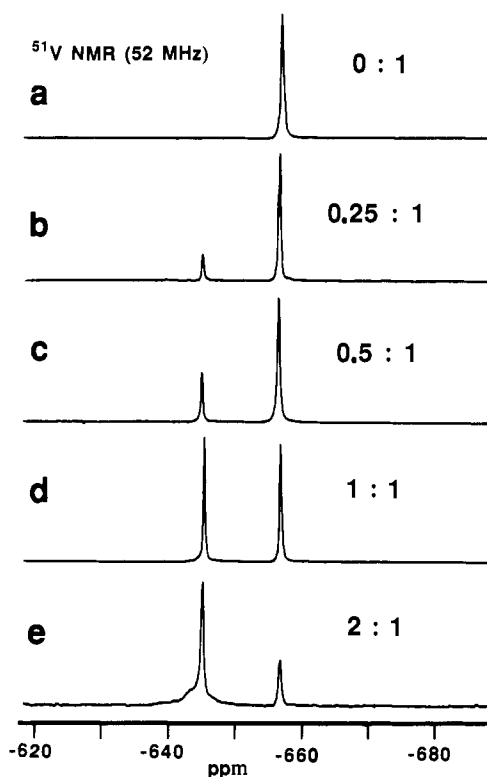
increasing the viscosity of the ambient-temperature sample by adding polystyrene and indeed a decrease in the ambient-temperature line width of the α-carbon was observed. The presence of two α-carbon signals is only seen when *exo*-norborneol is the substituent. The *exo*-norborneol was a racemic mixture, and the possibility that these two signals are due to the pairs (+, +, +)/(-, -, -) and (+, +, -)/(+, -, -) of diastereomers was eliminated, since no chemical shift differences could be observed by <sup>51</sup>V NMR for this system. As we show below, with enantiomerically pure borneol as the substituent, one <sup>51</sup>V NMR signal was observed, whereas two chemical resonances were observed when the other enantiomer is added to the system.

**Structural Characterization in the Solid State.** Mass spectrum analysis yielded molecular ions corresponding to the molecular weight of the monomer. However, it must be noted that only a molecular ion corresponding to VO(OCH<sub>3</sub>)<sub>3</sub> was observed despite the fact that this species is known to be a polymer in the solid state. IR spectroscopy yielded the ν<sub>V=O</sub> stretch from 999 to 1004 cm<sup>-1</sup> as observed previously for other vanadium alkoxides.<sup>37</sup> Although we have attempted to grow X-ray quality crystals of all these derivatives, no crystals with easily solvable diffraction patterns have been prepared. The few reported structures with the general formula VO(OR)<sub>3</sub> in the literature where R is an alkyl group testify in favor of the difficulties one encounters in characterization of these compounds with X-ray crystallography.<sup>16,18</sup> We have therefore resorted to extensive solution studies of the materials that were not accessible by X-ray crystallography in the solid state.

**Hydrolysis Studies.** Although oxovanadium(V) alkoxides hydrolyze easily, very little is known about the mechanism or rates of hydrolysis of these compounds. Aqueous studies suggest facile formation, as well as the hydrolysis, of mono- and dialkyl vanadates.<sup>15c</sup> We examined the hydrolysis of oxovanadium(V) tri-1-adamantoxide in CHCl<sub>3</sub>. At low water concentrations the reaction can be described by (9), whereas at high water concentrations a precipitate forms (eq 10). Presumably the precipitate is VO-



(OR)(OH)<sub>2</sub> and species derived from this compound, since such materials are likely to be much less soluble in CHCl<sub>3</sub>. The hydrolysis reaction was followed conveniently by <sup>51</sup>V NMR because a chemical shift of -658 ppm is observed for VO(O-1-Ad)<sub>3</sub> and a chemical shift of -646 ppm for VO(O-1-Ad)<sub>2</sub>OH (Figure 4). Figure 4 shows the spectra recorded of solutions containing 0, 0.25, 0.5, 1.0, and 2.0 equiv of H<sub>2</sub>O. A solution containing two <sup>51</sup>V NMR resonances was evaporated to dryness and the mass spectrum showed a molecular ion peak for the VO(O-1-Ad)<sub>2</sub>OH unit. This ion was not observed in mass spectra of water-free VO(O-1-Ad)<sub>3</sub>. Table II shows the concentrations calculated from <sup>51</sup>V NMR spectra of solutions containing from 0.1:1 to 0.7:1 equiv of water to vanadium. No precipitates formed in solutions with less than 1 equiv of added water, thus <sup>51</sup>V NMR spectra for quantization of these solutions could be recorded. Since the total vanadium concentrations are known, the concentrations of the



**Figure 4.** <sup>51</sup>V NMR spectra (52 MHz) of VO(O-1-Ad)<sub>3</sub> with added H<sub>2</sub>O. The solution has (a) no added H<sub>2</sub>O, (b) 0.25 equiv of H<sub>2</sub>O, (c) 0.5 equiv of H<sub>2</sub>O, (d) 1 equiv of H<sub>2</sub>O, and (e) 2 equiv of H<sub>2</sub>O. The solutions of samples recorded in (b)–(d) were all yellow, whereas the solution of the sample leading to spectrum a was colorless. Significant precipitates were observed in the solutions leading to spectra d and e.

VO(O-1-Ad)<sub>3</sub> and VO(O-1-Ad)<sub>2</sub>OH can be calculated from the <sup>51</sup>V NMR spectra. If all the H<sub>2</sub>O is free or present as hydrolysis product and the total H<sub>2</sub>O concentration is known, the free H<sub>2</sub>O concentrations can be calculated. Accordingly the concentration of free ROH can be calculated and equals the concentration of triester that has hydrolyzed. The hydrolysis constant of triester is defined in (11). Table II shows only the concentrations of

$$K_{\text{hyd}} = \frac{[\text{VO(O-1-Ad)}_2\text{OH}][\text{ROH}]}{[\text{VO(O-1-Ad)}_3][\text{H}_2\text{O}]} \quad (11)$$

various species determined experimentally with water concentrations of less than 1 equiv of the oxovanadium derivative, because once precipitation occurs quantification is no longer possible in the manner described above. The accuracy of these measurements is not as high as that of analogous studies in aqueous solutions given the high volatility of CHCl<sub>3</sub> and the difficulty in maintaining a constant 10 mM H<sub>2</sub>O concentration in the stock CHCl<sub>3</sub> solution. From (11), the hydrolysis constant was calculated, resulting in an average constant of 0.4 (±0.1).

The hydrolysis constant suggests that the stability of VO(O-1-Ad)<sub>3</sub> is comparable with that of VO(O-1-Ad)<sub>2</sub>OH, although the trialkoxide may be a bit more stable. This observation appears at first surprising considering the known water sensitivity of the

(37) Voronkov, M. G.; Shergina, N. I.; Lapsin, A. F. *Izv. Akad. Nauk. SSSR. Ser. Khim* 1972, 2812–4.

**Table III.**  $^{51}\text{V}$  NMR Chemical Shifts of Oxovanadium(V) Trialkoxides and Their Corresponding Monohydroxo Hydrolysis Products<sup>a</sup>

alcohol/solvent HOR	chemical shift, ppm		
	$\text{VO}(\text{OR})_3$	$\text{HO}-\text{VO}(\text{OR})_2$	concn, mM
isopropyl alcohol/ $\text{CHCl}_3$	-626	-629 <sup>b</sup>	150
cyclohexanol/hexanes	-627	-625	50
<i>tert</i> -butyl alcohol/ $\text{CHCl}_3$	-673	-659	50
cyclohexanol/ $\text{CHCl}_3$	-616	-620	50
HO-1-Ad/ $\text{CHCl}_3$	-658	-646	50
HO-1-Ad/ $\text{CH}_3\text{Ph}$	-661	-646	50
HO-2-Ad/ $\text{CHCl}_3$	-605	-612	50
HO-2-Ad/ $\text{CH}_3\text{Ph}$	-610	-616	50
<i>exo</i> -norborneol/ $\text{CHCl}_3$	-612	-604	50
<i>exo</i> -norborneol/hexanes	-620	-613	50
<i>endo</i> -norborneol/ $\text{CHCl}_3$	-594	-601	50
<i>endo</i> -norborneol/hexanes	-596	-604	50
triphenylmethanol/toluene	-728	-729	50
( <i>R</i> )-borneol/ $\text{CHCl}_3$	-592	-603	50
( <i>R</i> )-borneol/hexanes	-599	-607	50
( <i>S</i> )-borneol/ $\text{CHCl}_3$	-592	-603	50
( <i>S</i> )-borneol/hexanes	-598	-606	50

<sup>a</sup>The  $^{51}\text{V}$  NMR spectra were recorded at ambient temperatures at either 52 or 79 MHz with sweep widths around 15 000–20 000 Hz, a pulse width of 90°, and no relaxation delays. <sup>b</sup>The chemical shift of this species is estimated, since only a shoulder was observed at 53 MHz.



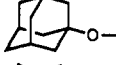
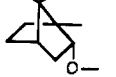
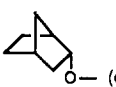
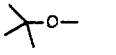
trialkoxides. These results are nevertheless consistent because hydrolysis forms materials that are no longer soluble in  $\text{CHCl}_3$ . The observed hydrolytic instability of trialkoxides may therefore merely be a result of the removal of a hydrolysis product from solution. Oxovanadium trialkoxides would be quite stable if hydrolysis would generate materials soluble in the particular solvent.

The reversibility of the trialkoxide hydrolysis reaction (eq 9) in organic solvents was explored by taking a solution containing 57 mM  $\text{VO}(\text{O}-1\text{-Ad})_3$  and 43 mM  $\text{VO}(\text{O}-1\text{-Ad})_2\text{OH}$ , recording a  $^{51}\text{V}$  NMR spectrum, and subsequently adding 400 mM HO-1-Ad. The  $^{51}\text{V}$  NMR spectrum of the solution containing the oxovanadium(V) alkoxides and the additional alcohol showed almost complete conversion (>98%) to the trialkoxide. This finding suggests that the hydrolysis of trialkoxides could be prevented if additional alcohol is added or, alternatively, the materials are studied in alcoholic solvents. Application of these reagents in organic synthesis using alcoholic solvents would be quite convenient since the hydrolytic lability is minimized.

Analogous reversibility experiments were conducted with the oxovanadium(V) triisopropoxide. Once 2 equiv of  $\text{H}_2\text{O}$  are added to a solution of 100 mM oxovanadium(V) triisopropoxide a yellow precipitate forms, but no additional resonances are observed in the  $^{51}\text{V}$  NMR spectrum. Similar results were obtained when less than 1 equiv of  $\text{H}_2\text{O}$  was added to the solution of oxovanadium(V) triisopropoxide. No hydrolyzed species was observed by  $^{51}\text{V}$  NMR for this compound at 52 or 79 MHz; presumably the chemical shifts of the tri- and diesters are superimposed. If additional pure isopropyl alcohol was added to the yellow suspension of  $\text{VO}(\text{OiPr})_3$  and precipitate, the solid redissolved and generated a colorless solution that was shown by  $^{51}\text{V}$  NMR spectroscopy to contain only  $\text{VO}(\text{OiPr})_3$ . We conclude that the hydrolysis products of  $\text{VO}(\text{OiPr})_3$  do not have  $^{51}\text{V}$  NMR chemical shifts sufficiently separated from  $\text{VO}(\text{OiPr})_3$ , which would allow direct observation by  $^{51}\text{V}$  NMR spectroscopy. Nevertheless, the hydrolysis reactions of  $\text{VO}(\text{OiPr})_3$  are reversible as shown for  $\text{VO}(\text{O}-1\text{-Ad})_3$ .

The first hydrolysis products of oxovanadium(V) trialkoxide derivatives are easily observed in the  $^{51}\text{V}$  NMR spectrum when the alkyl group is fairly bulky (Table III). The chemical shift of the monohydroxo compound can appear at either higher or lower field than that of the trialkoxide depending on alcohol and solvent. Oxovanadium(V) tricyclohexyl oxide, for example, is at -616 ppm in  $\text{CHCl}_3$  and -627 ppm in hexanes. The hydrolysis product for oxovanadium(V) tricyclohexyl oxide, on the other

**Table IV.**  $^{13}\text{C}$  Chemical Shifts of the  $\alpha$ -Carbons in  $\text{VO}(\text{OR})_3$  and Their Hydrolysis Products<sup>a</sup>

RO-	$\text{VO}(\text{OR})_3$ $\alpha$ -carbon, ppm	$\text{VO}(\text{OR})_2\text{OH}$ $\alpha$ -carbon, ppm	$\Delta\delta$
 (exo)	93.1	95.8	2.7
	93.9	96.4	2.5
	83.5	86.7	3.2
	97.5	100.4	2.9
	91.9	94.7	2.8
	83.9 <sup>b</sup>	86.9 <sup>b</sup>	3.0
	83.7 <sup>c</sup>	86.2 <sup>c</sup>	2.5

<sup>a</sup>The 75-MHz  $^{13}\text{C}$  spectra were recorded at ambient temperature, a pulse width of 30°, a sweep width of 20 000 Hz, a relaxation time of 1.0 min, and from 200–400 accumulations. <sup>b</sup>This work. <sup>c</sup>These chemical shifts were reported for  $^{13}\text{C}$  chemical shifts in a sample of  $\text{VO}(\text{O}-t\text{-Bu})_3$ . Witke, K.; Lachowitz, A.; Bruser, W.; Zeigan, D. Z. *Anorg. Allg. Chem.* **1980**, *465*, 193–203.

hand, appears at -620 ppm in  $\text{CHCl}_3$  and -625 ppm in hexanes. A list of chemical shifts for the new oxovanadium(V) derivatives described in this work, their corresponding monohydroxo compound, and the solvent these were recorded in are shown in Table III. The  $^{13}\text{C}$  chemical shift of the  $\alpha$ -carbon in the trialkoxy and monohydroxy compounds are shown in Table IV. In general, the  $^{51}\text{V}$  NMR chemical shifts of these compounds are separated by 2–15 ppm and the  $\alpha$ -C chemical shifts separated by 2–3 ppm. If the complexes otherwise are pure, their presence is easily observable by using both  $^{51}\text{V}$  and  $^{13}\text{C}$  NMR spectroscopy.

Comparison of the stability exhibited by trialkyl, dialkyl, and monoalkyl vanadates in aqueous solutions with that of oxovanadium(V) alkoxides in organic solvents is now possible. Aqueous solutions favor the hydrolyzed species, and it is rare to observe a trialkyl vanadate form in aqueous solution even with multifunctional ligands.<sup>38</sup> In aqueous solution, the water participates in the reaction and thus shifts the equilibrium toward the monoalkyl and dialkyl vanadates. Alcoholic solvents favor the trialkyl vanadium derivatives. The fact that concentrated alcoholic solutions favor trialkyl and dialkyl vanadates over monoalkyl vanadates may simply reflect that the alcohol participates in the reaction.<sup>34</sup> Organic solvents such as  $\text{CHCl}_3$  and toluene do not participate in the reaction, and the stability of the vanadium compounds in these solutions is a true measure of the inherent stability of the compounds. The studies presented in this paper suggest that the equilibria observed in aqueous and alcoholic solutions are merely a result of Le Chatelier's principle and do not reflect the inherent stability of trialkyl vanadates (i.e., oxovanadium(V) trialkoxides), which, as shown in this work, suggests that the trialkyl vanadates are significantly more stable than recognized earlier.

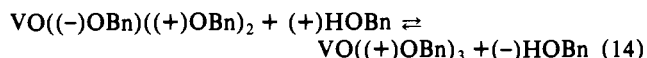
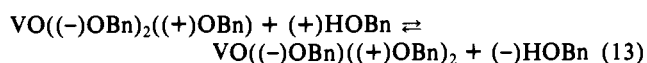
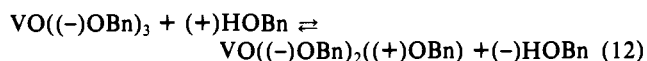
**Redox Stability of  $\text{VO}(\text{OR})_3$  Derivatives.** The reduction of  $\text{VO}(\text{O}-1\text{-Ad})_3$  was explored by using both electrochemical and chemical means. The vanadium in  $\text{VO}(\text{O}-1\text{-Ad})_3$  is apparently stabilized, because no reduction by electrochemical methods was observed even when the potential was brought to -2.3 V (in THF). Reduction was also attempted in  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ , and DMSO without success. Chemically, the  $\text{VO}(\text{O}-1\text{-Ad})_3$  was not reduced

(38) (a) Crans, D. C.; Shin, P. K. *Inorg. Chem.* **1988**, *27*, 1797–806. (b) Crans, D. C.; Ehde, P. M.; Shin, P. K.; Pettersson, L. *J. Am. Chem. Soc.* **1991**, *113*, 3728–36. (c) Tracey, A. S.; Gresser, M. J. *Inorg. Chem.* **1988**, *27*, 1269–75.

by triphenylphosphine even after storage for 2 weeks in a sealed NMR tube with  $\text{CHCl}_3$  in a 100 °C oven. The  $^{51}\text{V}$  NMR recorded at the end of 2 weeks showed only one resonance at -660 ppm compared to the one resonance at -660 ppm before the solution was heated.

Ascorbic acid and  $\beta$ -mercaptoethanol are known reductants of V(V), and indeed these compounds induced reduction of the vanadium. A solution of  $\text{VO}(\text{O-1-Ad})_3$  and ascorbic acid in a 1:1 ratio in  $\text{CH}_2\text{Cl}_2$  at ambient temperatures turns green over the course of 24 h and no  $^{51}\text{V}$  NMR signal is observed at the end of such treatment. In contrast, a pale yellow solution of 3 equiv of  $\beta$ -mercaptoethanol mixed with 1 equiv of  $\text{VO}(\text{O-1-Ad})_3$  in  $\text{CH}_2\text{Cl}_2$  immediately turned black and a black precipitate formed; this solution no longer has a  $^{51}\text{V}$  NMR signal.

**Transesterification Reactions of Chiral Oxovanadium(V) Trialkoxides.** The preparation of oxovanadium(V) tris[(1*R*)-endo-(+)-borneol]  $\text{VO}(+)\text{OBn}_3$  (**5**) and its enantiomer  $\text{VO}(-)\text{OBn}_3$  (**6**) have resulted in the first reports of chiral oxovanadium(V) trialkoxides. The transesterification reaction of **6** with (+)HOBn as shown by (**12**), (**13**), and (**14**) will generate oxovanadium(V) alkoxides containing the (+)OBn alkoxide. The



mixture of  $\text{VO}(-)\text{OBn}_3$  and (+)HOBn contains  $\text{VO}(-)\text{OBn}_3$  and its enantiomer  $\text{VO}(+)\text{OBn}_3$  as well as  $\text{VO}(-)\text{OBn}_2((+)\text{OBn})$  and its enantiomer  $\text{VO}(+)\text{OBn}_2(-)\text{OBn}$ . Since the two pairs of enantiomers are diastereomers, it should be possible to observe the two sets of enantiomers by  $^{51}\text{V}$  NMR spectroscopy if the chemical shifts are sufficiently different. A solution of  $\text{VO}(-)\text{OBn}_3$  (66 mM) in hexanes shows one major signal at -597.9 ppm with a minute shoulder at lower frequency (-596.8 ppm). Upon addition of (+)HOBn (66 mM) to the solution, the shoulder at -596.8 ppm increases. At a 1:1 ratio of (-)HOBn and (+)HOBn (that is 1:3 ratio of  $\text{VO}(-)\text{OBn}_3$  to (+)HOBn), the shoulder corresponds to 12% of total vanadium, and the  $\text{VO}(+)\text{OBn}_3$  and  $\text{VO}(-)\text{OBn}_3$  pair correspond to 88%. It therefore appears that the latter is significantly more stable than the former.

Using  $\text{Eu}(\text{thf})_3$ , we examined the purity of the (-)HOBn and found that the ligand contained only one enantiomer, corresponding to an ee of higher than 98 (supported by the rotation of the alcohol). The  $^{51}\text{V}$  NMR of the oxovanadium(V) trialkoxide of (-)HOBn, on the other hand, shows the presence of the other enantiomer, suggesting that the  $^{51}\text{V}$  NMR spectrum is more sensitive than  $\text{Eu}(\text{thf})_3$ . Chiral oxovanadium(V) trialkoxides show a greater stability for  $\text{VO}(-)\text{OBn}_3$  than  $\text{VO}(-)\text{OBn}_2((+)\text{OBn})$ . Such preferences could be used to develop a vanadium-based asymmetric catalyst for organic synthesis.

## Conclusion

A series of sterically hindered oxovanadium(V) alkoxides have been prepared by reacting  $\text{VOCl}_3$  with bulky alcohols. The steric bulk of the alcohol groups stabilize the oxovanadium(V) compound

with respect to redox and hydrolysis reactions such that the reactivity and properties of these species could be examined. The compounds appear to be monomeric in solution. The reaction of oxovanadium(V) alkoxo dichlorides with alcohol to form oxovanadium(V) dialkoxo chlorides and HCl is reversible, and the equilibrium favors the dichloride. The reaction of oxovanadium(V) dialkoxo chlorides with alcohol to form oxovanadium(V) trialkoxides and HCl is also reversible, with the equilibrium favoring the chloride. Preparation of the oxovanadium(V) trialkoxides therefore only proceed to completion when the HCl is removed during the reaction. The reversibility of these reactions suggests the application of  $\text{VO}(\text{OR})_2\text{Cl}$  or  $\text{VO}(\text{OR})\text{Cl}_2$  as reagents will generate the equilibrium mixture in the reaction solution within 30 min. The active oxidative catalyst may very well require that  $\text{VO}(\text{OR})_2\text{Cl}$ ,  $\text{VO}(\text{OR})\text{Cl}_2$ ,  $\text{VO}(\text{OR})_2(\text{OR})$ , and HCl are present in the solution before the desired transformation occurs. It is possible that the presence of HCl is particularly instrumental in the oxidative chemistry reported recently.<sup>23-30</sup>

Oxovanadium(V) trialkoxides are known to be very sensitive to moisture, but it was possible to study the first step of the hydrolysis reaction in organic solvents with these bulky vanadium derivatives. The addition of less than 1 equiv of  $\text{H}_2\text{O}$  to each oxovanadium(V) trialkoxide resulted in the formation of the first hydrolysis product  $\text{VO}(\text{OR})_2\text{OH}$ . This hydrolysis species is observed by both  $^{51}\text{V}$  and  $^{13}\text{C}$  NMR spectroscopy for the sterically hindered oxovanadium(V) alkoxides. Equilibrium studies showed that the  $\text{VO}(\text{OR})_3$  is not as unstable as anticipated but that its observed instability may be due to insolubility of the hydrolysis products of  $\text{VO}(\text{OR})_2\text{OH}$  under the reaction conditions and thus the removal of oxovanadium(V) derivatives by precipitation. Our studies suggest that oxovanadium(V) derivatives are hydrolytically stable in alcoholic solvents and thus convenient catalysts for synthetic reactions.

The first chiral oxovanadium(V) trialkoxides were prepared. The addition of an enantiomeric alcohol to a chiral oxovanadium(V) trialkoxide forms a diastereomeric oxovanadium(V) trialkoxide through the transesterification reaction. Both species can simultaneously be observed in a  $^{51}\text{V}$  NMR spectrum. Surprisingly, the oxovanadium(V) trialkoxides of all (+) or all (-) alcohols were 25-fold more stable than the oxovanadium(V) trialkoxides with (+, +, -) alcohols or (-, -, +) alcohols at ambient temperatures. This selectivity suggests that oxovanadium(V) trialkoxides of chiral alcohols may have potential use as chiral catalysts in, for example, allylic oxidations, epoxidations, or oxidative phenolic couplings.

Aqueous solutions do not generate significant concentrations of trialkyl vanadates and anhydrous ethanol or methanol solutions of vanadate contain trialkyl and dialkyl vanadates and very little monoalkyl vanadate. In both these solvents the solvent participates in the reaction, shifting the reaction in the direction of the trialkyl vanadate in the alcoholic solvent and in the direction of monoalkyl vanadate in water. Neither aqueous nor alcoholic solutions give a true estimate of the stability of these alkoxide compounds. It is revealing to discover that oxovanadium(V) trialkoxides and water are slightly more stable than  $\text{VO}(\text{OR})_2\text{OH}$  and ROH in  $\text{CHCl}_3$ , suggesting the gas-phase stability of these materials will mimic the observations made in organic solvents.

**Acknowledgment.** We thank Drs. Christopher R. Roberts, John B. Grutzner, and Christopher D. Rithner for helpful discussions.