Vanadyl Benzylphosphonates and Vanadyl Naphthylphosphonates: Intercalation Reactions with Butanols

Jack W. Johnson,* John F. Brody, and Robert M. Alexander

Corporate Research Laboratories, Exxon Research and Engineering, Annandale, New Jersey 08801

Boguslaw Pilarski and Alan R. Katritzky

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received November 8, 1989

Vanadyl organophosphonates of general formula $VO(RPO_3)\cdot xH_2O\cdot yC_2H_5OH$ have been synthesized by the reaction of V_2O_5 with RPO_3H_2 in refluxing ethanol (R = 1-naphthyl, 2-naphthyl, benzyl, *p*-chlorobenzyl, *p*-methylbenzyl, *p*-methoxybenzyl, α-methylbenzyl, 2,5-dimethylbenzyl, *p-tert*-butylbenzyl, benzoylmethyl, 1-naphthylmethyl, and 2-naphthylmethyl) and characterized by thermogravimetric analysis and X-ray powder diffraction. The new compounds exhibit layered structures that can be divided into groups according to the layer spacings observed. Benzylphosphonic, (*p*-chlorobenzyl)phosphonic, 2-naphthylphosphonic, and (benzoylmethyl)phosphonic acids form vanadyl compounds with structures in which the organic groups from adjacent layers interpenetrate, resulting in relatively small layer spacings, while the rest of the new compounds have structures in which the organic groups from adjacent layers abut, forming bilayers. Butanols undergo intercalation reactions resulting in expansion of the interlayer distance only in the former compounds, which possess layers of interdigitating organic groups.

Introduction

Layered solid compounds with alternating inorganic and organic layers are intriguing materials that can exhibit useful sorptive and catalytic properties and can serve as microcrystalline models for interfacial systems. Metal organophosphonates that crystallize in layered structures have recently been under intensive investigation. Organophosphonates of tetravalent metals such as zirconium ($M(RPO_3)_2\cdot nH_2O$) were the first to be studied in depth[1] and have been used as catalysts,[2] as ion exchangers,[3] and as materials for derivatizing electrode surfaces.[4] More recently, a variety of divalent metal organophosphonates ($MRPO_3\cdot nH_2O$) has been synthesized and structurally characterized.[5] Vanadyl organophosphonates ($VORPO_3\cdot nH_2O$) are layered inorganic/organic hybrids that can incorporate alcohols through coordination intercalation reactions.[6] In this intriguing series of layered compounds, the intercalating alcohol molecules are coordinated to vanadium atoms in the inorganic layer. These vanadium atoms are surrounded by phosphorus atoms bearing organic groups. The size and nature of these organic groups constrain the range of alcohol molecules that can be absorbed by means of the coordinative intercalation reaction. Earlier work from these laboratories showed that varying the organic group from phenyl to alkyl had a pronounced effect on the alcohol absorption properties of the vanadyl organophosphonates. In this report, we describe a more detailed study of the synthesis of vanadyl organophosphonates containing benzyl and naphthyl groups and their alcohol intercalation reactions.

Experimental Section

X-ray powder diffraction patterns were measured with a Siemens D-500 instrument using Cu Kα radiation at a scan rate of 1.2°/min. Thermogravimetric analyses were performed using a Du Pont 951/1090 thermal analysis unit. Weight-loss temperatures (T_n) reported are taken from the positions of the peaks in the DTG scan. The samples were heated at 10 °C/min in flowing He to 600 °C, cooled, and reheated at the same rate to 600 °C in air to oxidize the residue to $VOPO_4$. The formula weight of the starting material was then calculated from the known weight of $VOPO_4$ produced. The alcohols and V_2O_5 were reagent grade, and the phosphonic acids were synthesized via Arbusov reactions as reported elsewhere.[7]

Synthesis. Vanadyl organophosphonates were prepared by refluxing finely ground vanadium pentoxide with various phosphonic acids in 95% EtOH. The molar ratio of phosphonic acid to V_2O_5 was adjusted to 2.4:1, giving a 20% excess of phosphorus to vanadium in the reaction mixture. The reactions contained a two-phase liquid–solid mixture throughout the course of the reaction, beginning with the characteristic rust-orange color of V_2O_5 and progressing to a gray, green, or aqua color. The reactions were continued until no noticeable color change was observed for 2 or 3 days. At that time the product was separated by filtration and analyzed by X-ray diffraction. If the resulting diffraction pattern revealed the presence of V_2O_5, the product was ground, recombined with its filtrate, and refluxed for another week. Microanalytical results were obtained from Galbraith Laboratories and generally showed stoichiometries approaching P/V = 1; however, complete reaction of the V_2O_5 was difficult to achieve.

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0897-4756/90/2802-0198$02.50/0

Table I. Vanadyl Organophosphonates

compound	layer spacing, Å	n^a	% yield	reaction time, days	$T_1{}^b$	$T_2{}^b$
$VO(C_6H_5CH_2PO_3)\cdot H_2O\cdot 0.5C_2H_5OH$ (**1**)	11.96/8.92[c]	4/5	101	11	120	300
$VO(p\text{-}ClC_6H_4CH_2PO_3)\cdot H_2O\cdot C_2H_5OH$ (**2**)	13.65	4	94	6	120	240
$VO(p\text{-}CH_3C_6H_4CH_2PO_3)\cdot H_2O$ (**3**)	15.48	8	96	7		260
$VO(2,5\text{-}(CH_3)_2C_6H_3CH_2PO_3)\cdot H_2O$ (**4**)	15.09	4	95	7		240
$VO(p\text{-}(CH_3)_3CC_6H_4CH_2PO_3)\cdot 2H_2O$ (**5**)	15.92	5	98	14	70	180/230[d]
$VO(p\text{-}CH_3OC_6H_4CH_2PO_3)\cdot H_2O$ (**6**)	17.79	4	103	10		270
$VO(C_6H_5CH(CH_3)PO_3)\cdot H_2O$ (**7**)	14.49	3	82	23		260
$VO(C_6H_5COCH_2PO_3)\cdot 2H_2O$ (**8**)	11.0/10.28[c]	1/5	79	23		280
$VO(2\text{-}C_{10}H_7CH_2PO_3)\cdot H_2O$ (**9**)	16.08	4	96	10		270
$VO(1\text{-}C_{10}H_7CH_2PO_3)\cdot H_2O$ (**10**)	11.2/19.9[c]	1/1	97	26		
$VO(2\text{-}C_{10}H_7PO_3)\cdot H_2O\cdot C_2H_5OH$ (**11**)	14.47	8	92	7	140	210
$VO(1\text{-}C_{10}H_7PO_3)\cdot H_2O$ (**12**)	15.96	7	83	15		260

[a] n = number of observed 00l lines used to calculate layer spacing. [b] T_1 and T_2 are temperatures (°C) of weight loss in thermogravimetric analysis. [c] Two phases observed in X-ray powder diffraction pattern. [d] Three-step weight loss observed in TGA.

Typical results are as follows: $VO(C_6H_5CH_2PO_3)\cdot H_2O$ (**1**, vacuum dried) anal. calcd 19.97% V, 12.14% P, 32.96% C, 3.56% H; found 20.67% V, 11.70% P, 32.85% C, 3.48% H; $VO(p\text{-}ClC_6H_4CH_2PO_3)\cdot H_2O\cdot C_2H_5OH$ (**2**) anal. calcd 15.18% V, 9.23% P, 32.21% C, 4.21% H; found 16.02% V, 8.94% P, 31.56% C, 4.04% H; $VO(p\text{-}CH_3C_6H_4CH_2PO_3)\cdot H_2O$ (**3**) anal. calcd 18.93% V, 11.51% P, 35.71% C, 4.12% H; found 20.07% V, 10.94% P, 35.10% C, 3.78% H.

Alcohol Intercalation. The newly synthesized vanadyl organophosphonate compounds were treated with normal and secondary butyl and isobutyl alcohols at both ambient and elevated temperatures. Separate samples (0.250–0.500 g) of vanadyl organophosphonate were stirred in each of the three butanols. After being stirred for 16 h, the samples were separated by filtration and analyzed by X-ray diffraction. These three samples were then treated again with their respective butanols. The secondary butyl alcohol and isobutyl alcohol mixtures were refluxed (bp 98 and 108 °C) while the n-butyl alcohol mixture was maintained at 100 °C for 16 h. These samples were cooled, separated by filtration, and analyzed by X-ray diffraction.

Results

Synthesis. Vanadyl organophosphonates are synthesized by refluxing vanadium pentoxide with an organophosphonic acid in alcoholic solution. The vanadium is reduced from V^{5+} to V^{4+} by the alcohol, which is oxidized to aldehyde. The product precipitates as a blue to blue-green solid as the reaction proceeds according to eq 1.

$$V_2O_5(s) + 2RPO(OH)_2(soln) + 3C_2H_5OH \xrightarrow[\text{reflux}]{} 2VORPO_3\cdot H_2O\cdot C_2H_5OH(s) + CH_3CHO + H_2O \quad (1)$$

Previous work has shown[6] that when R is an n-alkyl or an aryl group such as phenyl or p-methoxyphenyl, one molecule of ethanol per formula unit is included in the product. This alcohol is subject to exchange reactions with other alcohols and with water. The various vanadyl benzyl- and naphthylphosphonates listed in Table I have been synthesized by this route. Thermogravimetric analysis shows that some contain ethanol and that some contain only one or two molecules of water per formula unit, depending on the identity of the organic group.

Vanadyl benzylphosphonate (**1**) is obtained as a mixture of two phases, one with a layer spacing of 12.0 Å and the other with a layer spacing of 8.9 Å. The ethanol-containing phase, $VO(C_6H_5CH_2PO_3)\cdot H_2O\cdot C_2H_5OH$, has the larger layer spacing. Loss of alcohol results in a phase with a layer spacing reduced by 3.1 Å. When the mixed phase is evacuated at 100 °C, the pure 8.9-Å phase is formed, as demonstrated by X-ray diffraction and elemental analysis. Thermogravimetric analysis of the two-phase product shows that the first weight loss, centered at 120 °C, is about 8 wt %, while the calculated loss from the formula $VO(C_6H_5CH_2PO_3)\cdot H_2O\cdot C_2H_5OH$ is 15.3 wt %. The mixture is thus about half $VO(C_6H_5CH_2PO_3)\cdot H_2O$ as suggested by the similar relative intensities of the lines for the two phases in the powder diffraction pattern.

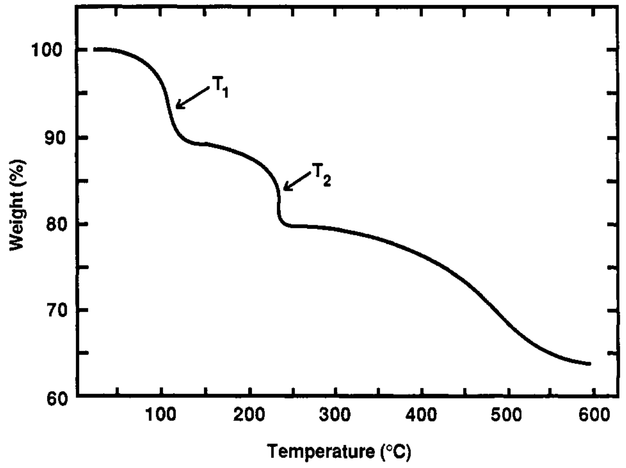

Figure 1. Thermogravimetric analysis of $VO(p\text{-}ClC_6H_4CH_2PO_3)\cdot H_2O\cdot C_2H_5OH$ (**2**) in flowing helium; heating rate 10 °C/min.

The p-chloro derivative, $VO(p\text{-}ClC_6H_4CH_2PO_3)\cdot H_2O\cdot C_2H_5OH$ (**2**), is isolated as a single phase, as is shown by its X-ray powder diffraction pattern. The TGA, displayed in Figure 1, shows a two-stage weight loss, with a first step centered at T_1 = 120 °C representing loss of ethanol and a second step centered at T_2 = 240 °C representing the loss of a water molecule. Above 400 °C further weight is lost as the chlorobenzyl group decomposes. The formula weight determined from the oxidation to $VOPO_4$ is 337, which agrees well with the value of 335.6 calculated from the formula. Elemental analysis also confirms the stoichiometry of one alcohol molecule per formula unit. When a sample of **2** is heated at 100 °C in vacuo for 1 day, the ethanol is removed. The resulting alcohol-free phase $VO(p\text{-}ClC_6H_4CH_2PO_3)\cdot H_2O$ has a layer spacing of 11.66 Å.

All of the compounds of Table I show the loss of a water molecule in the TGA in the temperature range 200–300 °C. Some of them also display a lower temperature weight loss due either to intercalated ethanol (**1**, **2**, **11**) or to an additional water molecule (**5**). All compounds show low-angle diffraction maxima in their X-ray powder patterns that are typical of layered phases. Most compounds exhibit a series of sharp lines corresponding to the layer spacing, as well as some additional lines we have not been able to index, indicating that the microcrystalline particles are ordered. However, in contrast to the results seen in the series of vanadyl alkylphosphonates and vanadyl arylphosphonates, the layer spacings observed (Figure 2) in this series of vanadyl benzylphosphonates do not correlate regularly with the size of the substituted benzyl

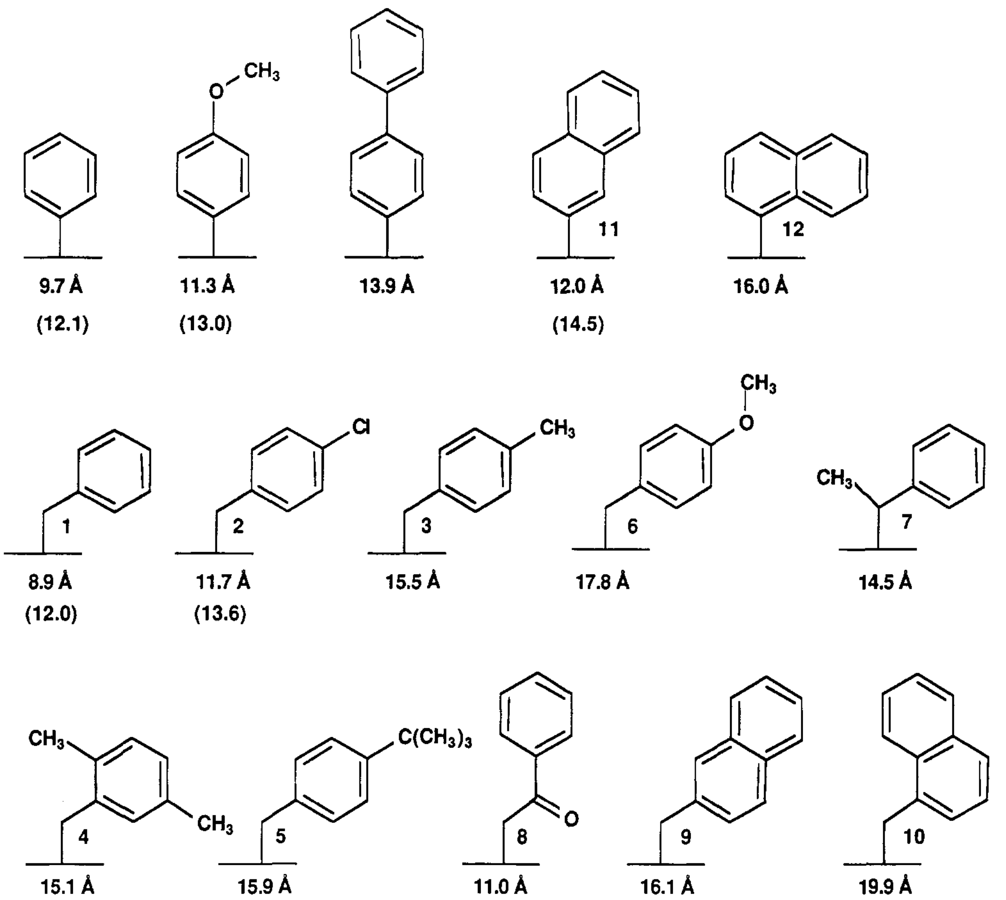

Figure 2. Layer spacings of $VO(RPO_3){\cdot}H_2O$ for various R groups. Values in parentheses are for ethanol-containing phases.

group. For example, since the size of methyl and chloro substituents are similar, we expect the layer spacings of the vanadyl chloro- and methylphosphonates **2** and **3** to be about the same, but they differ substantially at 13.65 and 15.48 Å, respectively. In addition, the smaller spacing compound **2** incorporates a molecule of ethanol in the formula unit while the larger spacing compound **3** does not. The X-ray data lead to the conclusion that the size and shape of the benzyl group not only affect the packing in the interlayer region but also affect the packing of vanadium atoms and phosphate groups in the covalently bound inorganic layer as well.

Alcohol Intercalation. The vanadyl benzylphosphonates and vanadyl naphthylphosphonates were treated with *n*-, *sec*-, and isobutyl alcohols at ambient temperature and at 100 °C. The *p*-methylbenzyl, *p*-methoxybenzyl, α-methylbenzyl, 2-naphthylmethyl, 1-naphthylmethyl, and 1-naphthyl derivatives (**3**, **6**, **7**, **9**, **10**, and **12**) were inert to all three alcohols at ambient temperature and at 100 °C. No significant change in these compounds was detected by X-ray diffraction after alcohol treatment. The 2,5-dimethylbenzyl derivative (**4**) did not react with the alcohols at ambient temperature, but at 100 °C it dissolved, leaving only trace amounts of a dark colored solid residue. These are the compounds of Table I that contain one molecule of water per formula unit after isolation from the ethanolic synthesis mixture.

The compounds that contain ethanol show more interesting behavior when treated with butanols. When vanadyl benzylphosphonate (**1**), which is a mixture of a 12.0-Å ethanol-containing phase and an 8.9-Å ethanol-free phase, is treated with any of the three butanols at ambient temperature, the relative amount of the 8.9-Å phase increases at the expense of the 12.0-Å phase. When treated at 100 °C, all of the ethanol is removed and a pure 8.9-Å phase results. No butanol intercalates are formed under these conditions; rather, ethanol is extracted from the solid by the butanol, leaving an alcohol-free phase. Vanadyl (*p*-chlorobenzyl)phosphonate (**2**) did not react with any butanol at ambient temperature but at 100 °C formed an intercalate with *n*-butanol that exhibited a layer spacing of 15.14 Å. TGA indicated the incorporation of ~0.8 equiv of butanol per formula unit. The original 13.65-Å ethanol-containing phase was also present in a minor amount. When **2** was treated with iso- and *sec*-butyl alcohols at 100 °C, the sample dissolved.

Treatment of 2-naphthylphosphonate (**11**) with *n*-butanol at ambient temperature yielded a single-phase *n*-butanol intercalate with a 16.87-Å layer spacing. It was well-ordered, with eight orders of the layer spacing observed in the powder diffraction pattern. Examination by TGA indicated a butanol content of slightly greater than 0.8 equiv per formula unit. When **11** was treated with isobutyl alcohol at room temperature, a minor phase (about 10–15%) with an expanded layer spacing of 17.1 Å was observed along with the unchanged 14.5-Å ethanol-containing starting phase. When the isobutyl alcohol treatment was done at 100 °C, a well-ordered expanded phase with a 15.7-Å layer spacing was observed, along with a minor (~10%) 12.1-Å phase. The isobutyl alcohol content was estimated by TGA as 0.6 equiv per formula unit. Treatment of **11** with *sec*-butyl alcohol at room temperature gave again a 17.0-Å expanded phase as a minor (15%) product along with unchanged starting material. Treatment at 100 °C resulted in a major phase with a layer spacing of 11.9 Å and indication of several minor expanded phases of less than 10% relative intensity at 13.6, 15.5, and 20.9 Å. The *sec*-butyl alcohol content was only ~0.15

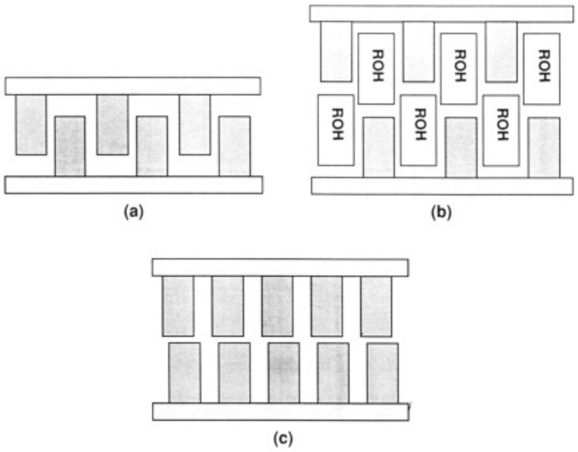

Figure 3. Schematic representation of the packing of the organic groups in vanadyl organophosphonates: (a) inderdigitating R groups; (b) inderdigitating R groups as in (a) with intercalated alcohol molecules; (c) abutted R groups in bilayer arrangement.

equiv per formula unit. The ~12-Å phase observed after 100 °C treatment in both cases is the ethanol-free $VO(2\text{-}C_{10}H_7PO_3)\cdot H_2O$. Indeed, when **11** is dried at 100 °C in vacuo, the same 12.0-Å phase is obtained.

Vanadyl (*p*-tertbutylbenzyl)phosphonate (**5**) intercalates *n*-butyl alcohol at ambient temperature to give an 18.18-Å product contaminated by a minor amount of 15.9-Å starting material. With isobutyl alcohol at room temperature, **5** gives a similar intercalate with a layer spacing of 17.2 Å. Treatment at 100 °C with these two alcohols causes **5** to dissolve. Due to its limited crystallinity and two-phase nature, the benzoylmethyl derivative (**8**) was not examined further.

Discussion

The compounds represented in Figure 2 can be divided into groups based on their observed layer spacings. The 2-naphthylphosphonate derivative (**11**) fits nicely into the previously reported aryl series of compounds composed of vanadyl phenyl-, (*p*-methoxyphenyl)-, and *p*-biphenylphosphonate. However, vanadyl 1-naphthylphosphonate (**12**) has a larger layer spacing than would be expected from the vertical extension of its organic group and must have an intralayer arrangement of vanadyl and phosphonate groups that differs from that of the other aryl derivatives. Indeed, as the lateral area occupied by the organic group on the layer surface increases, different layer structures will be required to accommodate the enforced larger spacings between phosphorus atoms.

The benzyl derivatives **1** and **2**, and the benzoyl derivative **8** have relatively small layer spacings. **1** and **2** intercalate alcohols, as do members of the vanadyl arylphosphonate series. While the details of the layer structures of these two sets of compounds cannot be identical (vanadyl benzyl- and (*p*-chlorobenzyl)phosphonate have larger organic groups but smaller layer spacings than vanadyl phenyl- and (*p*-methoxyphenyl)phosphonate), they must each have structures in which the organic groups from adjacent layers interdigitate. This arrangement facilitates alcohol intercalation, as shown schematically in Figure 3. In contrast, the larger spacings of **3–7**, **9**, **10**, and **12** indicate that the organic groups from adjacent layers abut one another, forming a bilayer arrangement (Figure 3c). In this arrangement, alcohol molecules do not have access to vanadium coordination sites on the surface of the layers.

Vanadyl organophosphonates with normal alkyl groups or with phenyl or *p*-methoxyphenyl groups bound to phosphorus intercalate alcohol molecules. The vanadyl alkylphosphonates rapidly intercalate both *n*-butyl and isobutyl alcohols rejecting *sec*-butyl alcohol, while the arylphosphonates intercalate *n*-butyl alcohol readily, isobutyl alcohol only partially, and *sec*-butyl alcohol not at all. Compounds in these two series exhibit layer spacings that increase regularly with the size of the organic groups, suggesting a structure in which organic groups from adjacent layers interpenetrate in the interlayer region and an intralayer arrangement of vanadium and phosphate that remains constant as the size of the organic groups is varied. These compounds do not dissolve in alcohol solutions at temperatures as high as 100 °C. In contrast, the new vanadyl organophosphonates reported in this paper that incorporate benzyl or naphthyl groups bound to phosphorus seem to have a variety of packing arrangements, resulting in layer spacings that are not readily interpretable by using simple models of molecular size. Many of the new compounds do not intercalate alcohols at all, and others dissolve when heated in butanol. Only the *p*-chlorobenzyl, *p*-*tert*-butylbenzyl, and 2-naphthyl derivatives (**2**, **5**, and **11**) intercalate butanols, with **2** and **5** dissolving at 100 °C. While the dissolution reaction is interesting in its own right, no evidence was observed for the formation of suspensions of extended vanadium phosphonate layers. As the bulk of the organic groups on phosphorus increases, soluble globular molecular species are favored over stable, insoluble solid layers, resulting in relative weakness in intralayer V–O–P bonding. The only compound that cleanly makes single-phase alcohol intercalates at room temperature is vanadyl 2-naphthylphosphonate (**11**), and its selectivity in alcohol reactions is similar to that of the previously reported[6] vanadyl arylphosphonates $VO(C_6H_5PO_3)\cdot H_2O$ and $VO(p\text{-}CH_3OC_6H_4PO_3)\cdot H_2O$. The steric nature of a 2-naphthyl group in this context is more similar to that of a phenyl group than to that of a 1-naphthyl or of any substituted benzyl group, due to the limited spatial extension of the 2-naphthyl group in the direction perpendicular to the P–C bond. Thus, we should expect the intercalation chemistry of vanadyl phenylphosphonate, which is controlled by the interlayer packing, to be more similar to that of vanadyl 2-naphthylphosphonate (**11**) than to that any of the other compounds of this report.

Acknowledgment. We thank D. Rasala for the preparation of (α-methylbenzyl)phosphonic acid.

Registry No. **1**, 125593-70-6; **2**, 125593-72-8; **2**·0.8*n*-butyl alcohol, 125593-83-1; **3**, 125593-73-9; **4**, 125593-74-0; **5**, 125593-75-1; **5**·*xn*-butyl alcohol, 125593-88-6; **5**·*x*isobutyl alcohol, 125593-89-7; **6**, 125593-76-2; **7**, 125610-33-5; **8**, 125593-77-3; **9**, 125593-78-4; **10**, 125593-79-5; **11**, 125593-81-9; **11**·0.8*n*-butyl alcohol, 125593-84-2; **11**·0.6isobutyl alcohol, 125593-85-3; **11**·0.15*sec*-butyl alcohol, 125593-86-4; V_2O_5, 1314-62-1; $C_6H_5CH_2PO_3H_2$, 6881-57-8; $p\text{-}ClC_6H_4CH_2PO_3H_2$, 39225-05-3; $p\text{-}CH_3C_6H_4CH_2PO_3H_2$, 13081-74-8; $2,5\text{-}(CH_3)_2C_6H_3CH_2PO_3H$, 125593-67-1; $p\text{-}(CH_3)_3CC_6H_4CH_2PO_3H_2$, 125593-68-2; $p\text{-}CH_3OC_6H_4CH_2PO_3H_2$, 40299-61-4; $C_6H_5CH(CH_3)PO_3H_2$, 61470-40-4; $C_6H_5COCH_2PO_3H_2$, 4724-50-9; $2\text{-}C_{10}H_7CH_2PO_3H_2$, 16672-84-7; $1\text{-}C_{10}H_7CH_2PO_3H_2$, 4730-77-2; $2\text{-}C_{10}H_7PO_3H_2$, 21521-77-7; $1\text{-}C_{10}H_7PO_3H_2$, 7402-93-9; *n*-butyl alcohol, 71-36-3; *sec*-butyl alcohol, 78-92-2; isobutyl alcohol, 78-83-1.