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Note

New chiral terpene-derived vanadatranes

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Abstract

The synthesis of three new chiral vanadatranes by reaction of oxovanadium(V) alcoholates with triethanolamine derivatives obtained from the terpenes (−)-β-pinene, (−)-limonene, and (−)-menthone is reported. Their structure is elucidated by NMR spectroscopy (^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{51}V).

Keywords: Chiral vanadatranes; Terpene derivatives; NMR spectroscopy (^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{51}V)

1. Introduction

Derivatives and analogues of triethanolamine often form cage compounds with both main group and transition metals. Such compounds have been called *atranes* (in the case of vanadium, vanadatranes). The parent compound vanadatrane was first obtained from triethanolamine and oxovanadium(V) alcoholates by Voronkov et al. [1] and shows interesting structural properties: it is a stable monomeric vanadium(V) alkoxide and not prone to oligomerization reactions as most oxovanadium alkoxides are when concentrated or crystallized.

Only very few chiral vanadatranes have been reported up to now; in these cases, one of the hydrogen atoms in all three CH_2–O groups of triethanolamine has been replaced by an alkyl or phenyl substituent. However, most of these compounds have been obtained solely in racemic form [2], and thus only four homochiral (optically active) vanadatranes are known [3]. In this work, we whish to present three new enantiopure chiral vanadatranes which are easily accessible from terpenes from the chiral pool. The ligands **2a**, **2b** and **2c** were prepared by ring opening of the corresponding homochiral epoxides **1a**, **1b** or **1c** with diethanolamine as previously described [4]. Their reaction with triethoxy vanadate in ethanol solution occurs smoothly at room temperature to give the corresponding vanadatranes **3a**, **3b** and **3c** as air-stable colourless to pale yellow solids (Fig. 1).

The vanadatranes were fully characterized by the usual techniques (microanalysis, mass spectrometry, IR and NMR spectroscopy). The presence of the oxovanadium(V) unit is clearly reflected in the typical IR signals at 955–965 (V=O) and 630–635 (V–O) cm^{-1} [2]. The existence of the V–N bond is shown by the close analogy of the ^{51}V, ^{17}O, and ^{15}N NMR data when compared with other vanadatranes whose crystal structure [2,3] is known. Thus, simple oxovanadium(V) alcoholates show a highly shielded vanadium atom in organic solvents ($OV(OEt)_3$: δ −598 [5]; $OV(OPr^i)_3$: δ −628 [6]), while the vanadatranes **3** (δ −380.6, −400.4, and −392.7, respectively) compare well with the unsubstituted parent compound (δ −383.5 [2]). ^{15}N and ^{17}O NMR data were determined for the limonene-derived compound **3a**. The nitrogen chemical shift (δ 59.2, $CDCl_3$) is clearly distinguished from the uncoordinated ligand (δ 26.4) and reflects the presence of the vanadium–nitrogen bond, just as in the parent vanadatrane (δ 54.8, d_6-DMSO) and the corresponding free ligand triethanolamine (δ 24.7) [7]. The ^{15}N–^{51}V coupling is not resolved in the vanadatranes, but a coupling to the hydrogen atoms of the neighbouring methylene groups can be observed (5.5 Hz; parent vanadatrane: 3.2 Hz [7]). Up to now, ^{17}O NMR data of vanadatranes have always been measured in D_2O

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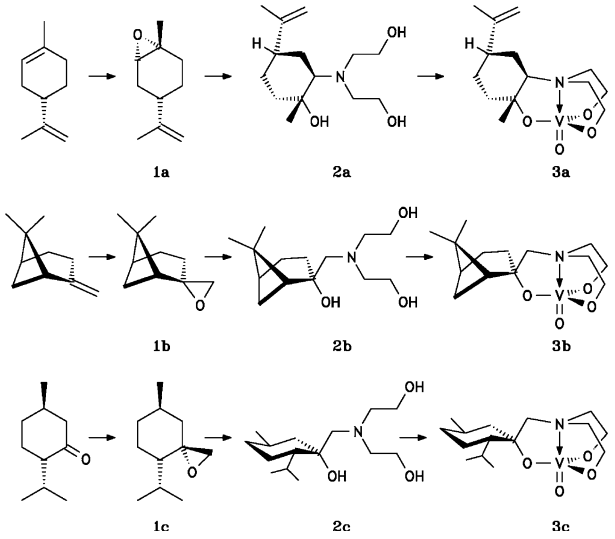

Fig. 1. Synthesis of the vanadatranes **3a**, **3b** and **3c**.

(preferably enriched in ^{17}O). As a result, rapid exchange of oxygen between vanadatrane and the solvent occurred, and two signals of the same intensity were observed (δ 980, $\Delta\nu$ 275 Hz (line width at half height); δ 954, $\Delta\nu$ 305 Hz) [5,8]. This observation was explained by partial hydrolysis of the vanadatrane in aqueous solution. One of the triethanolamine arms is detached and leaves behind an anionic vanadium complex with two oxygen atoms in non-equivalent positions which are responsible for the two signals observed. The oxygen atoms of the triethanolamine moiety do not exchange with ^{17}O labelled water and are therefore not observed. In contrast, we have measured the spectrum in $CDCl_3$ at natural ^{17}O concentration and found two well-resolved signals in a 3:1 ratio (δ 386, $\Delta\nu$ 1870 Hz (V–O); δ 1209, $\Delta\nu$ 370 Hz (V=O)), while the free ligand gives rise only to a very broad hump in the range of $+10$– -100 ppm. As for almost all oxygen atoms connected to another element by a double bond, a higher deshielding of the V=O oxygen atom in combination with a narrower line width is observed.

The structure of the terpene-derived part of compounds **3a**–**c** was studied by ^{1}H and ^{13}C NMR techniques, including two-dimensional shift correlations, and NOE determinations. Despite the comparatively strong overlap of the ^{1}H signals, the assignment including stereochemical aspects is complete for compound **3a**, and close to complete for **3b** and **3c**. Fig. 2 shows the numbering of the atoms quoted in the NMR spectra (see Section 2) for the limonene-derived compound **3a**. The numbering of **3b** and **3c** was made analogously and is consistent with that of the corresponding silatranes obtained with the same ligands [4].

As a rule, the conformations closely resemble those of the corresponding silatranes. Most of the conclusions drawn about their structures also apply here. Remarkable is the absence of strain in these molecules, since all ring systems are in conformations very similar to those in the parent terpenes. The main differences are due to the stronger deshielding effect of the vanadium(V) unit as compared to silicon; thus, in the ^{13}C spectra, the carbon atoms attached to oxygen show considerably higher deshielding in the vanadatranes ($\Delta\delta$ 13, ..., 20 ppm), while those attached to nitrogen are affected to a lesser extent ($\Delta\delta$ 1, ..., 3 ppm), and all other carbon atoms do not suffer any changes ($\Delta\delta \leq \pm 1$ ppm). An analogous effect is observed in the ^{1}H spectra, where the deshielding of protons in the O–C*H* units is more pronounced in the vanadium complexes ($\Delta\delta$ 0.5, ..., 0.8 ppm), whereas protons in N–C*H* feel less influence ($\Delta\delta$ 0.1, ..., 0.3 ppm). Interestingly, all signals of the terpene moieties show a tendency towards higher *shielding* in the vanadatranes ($\Delta\delta$ -0.2, ..., 0.0 ppm for **3a** and **3c**, $\Delta\delta$ -0.1, ..., -0.4 ppm for **3b**). The greater difference in the pinane residue in **3b** suggests that the conformation may be somewhat different from the corresponding silicon compound. The similarity of the NMR spectra of the vanadatranes and the silatranes includes the occurence of a very characteristic NOE effect in **3a** between the methyl group 11H and one proton of the N–CH_2 group (6H) which proves the puckering of the five-membered rings as depicted in Fig. 2 (right). Since signal overlap is more of a problem in the compounds **3b** and **3c**, one cannot draw the same conclusions about ring puckering with certainty in these cases.

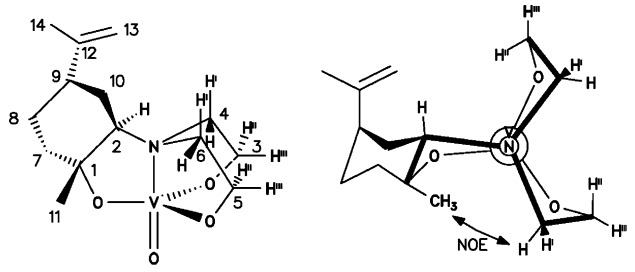

Fig. 2. NMR numbering of the atoms of **3a** and conformation in solution.

2. Experimental

The chiral triethanolamines **2a**, **2b** and **2c** were prepared as described [4]. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Optical rotations were measured with a Perkin–Elmer 241 M polarimeter and are quoted in 10^{-1} deg cm^2 g^{-1}. Mass spectra were obtained on a Trio 2000 instrument in EI mode. IR spectra (4000–400 cm^{-1}) were recorded on a Mattson 7000 FTIR instrument in KBr pellets. ^{1}H, ^{13}C, ^{15}N, ^{17}O, and ^{51}V NMR spectra were measured on Varian UNITY 300, Bruker AM 360 and Bruker DRX 500

spectrometers, all nuclei except ^{17}O at room temperature (r.t.), whereas ^{17}O was measured at 50 °C. For assignment of the ^{1}H and ^{13}C signals and conformational analysis, H,H-COSY with double quantum filter, HETCOR, HMQC, HMBC, and one dimensional NOE difference spectra were used. ^{51}V chemical shifts are given relative to neat $OVCl_3 = 0$ ppm, with half height line widths in parenthesis. ^{15}N and ^{17}O NMR spectra were measured in natural abundance in direct detection mode, using 1.5 M solutions of the compound. For ^{17}O NMR spectra, an aquisition time of 0.031 s and a relaxation delay of 0.002 s was applied. Chemical shifts are given relative to $H_2O = 0$ ppm. ^{15}N spectra were recorded after addition of $Cr(acac)_3$ (0.03 M) as relaxation reagent, using inverse gated decoupling, an acquisition time of 1 s and a relaxation delay of 3 s. Chemical shifts are given relative to nitromethane (50% in $CDCl_3$) = 379.6 ppm. Chemical shifts from the literature are converted to this scale.

A suspension of V_2O_5 (546 mg, 3 mmol) in dry EtOH (120 ml) was refluxed overnight, cooled to r.t. and filtered. The solid, assumed to be unchanged V_2O_5, was dried and weighted. From this weight, the amount of $OV(OEt)_3$ in the filtrate was calculated. Typically, solutions containing approximately 3 mmol of $OV(OEt)_3$ were obtained [9]. They were treated with a solution of one equivalent of the corresponding chiral triethanolamine in 5 ml of EtOH at r.t. for 2 h. Complex **3b** precipitates directly from the reaction mixture as a colourless powder which is filtered off and dried in vacuo. The complexes **3a** and **3c** are obtained as crystalline pale yellow solids upon slow evaporation of approximately 90% of the solvent, filtration and drying in vacuo.

*2.1. (3R,6S,8R)-5-Aza-3-methyl-6-(1-methylethenyl)-1-oxo-1-vanada-2,12,13-trioxatricyclo[7.3.3.0]^{3,8}pentadecane (**3a**)*

Yield: 530 mg (55%), m.p. 214 °C (dec.). IR (cm^{-1}): 965 s ν(V=O), 630 m ν(V–O). ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 3H, 11H), 1.49 (m, 1H, 7H ax.), 1.56 (m, 1H, 8H ax.), 1.60 (dm, 10.8 Hz, 1H, 7H eq.), 1.72 (s, 3H, 14H), 1.80 (td, 13.2 Hz, 5.7 Hz, 1H, 10H ax.), 1.99 (dm, 10.8 Hz, 1H, 8H eq.), 2.12 (dm, 13.5 Hz, 1H, 10H eq.), 2.51 (m, 1H, 9H eq.), 2.75 (dd, 13.2 Hz, 4.8 Hz, 1H, 6H′), 2.87 (td, 12.6 Hz, 5.7 Hz, 1H, 4H), 2.95 (dd, 13.2 Hz, 2.7 Hz, 1H, 2H ax.), 3.09 (dd, 12.9 Hz, 3.9 Hz, 1H, 4H′), 3.32 (td, 12.6 Hz, 6.6 Hz, 1H, 6H (NOE to 11H)), 4.38 (br, 1H, 3H‴), 4.57 (br, 1H, 5H‴), 4.60 (td, 12.0 Hz, 3.9 Hz, 1H, 3H″), 4.74 (td, 12.0 Hz, 4.2 Hz, 1H, 5H″), 4.80 (‘s’, 1H, 13-H *trans* to $CH_3$14), 4.93 (‘s’, 1H, 13H *cis* to $CH_3$14). ^{13}C NMR ($CDCl_3$): δ 22.6 (C14), 23.3 (C11), 25.1 (C10), 25.9 (C8), 38.6 (C9), 39.2 (C7), 50.7 (C6), 53.2 (C4), 62.6 (C2), 74.3 (C3), 75.5 (C5), 89.7 (C1), 111.2 (C13), 145.6 (C12). ^{51}V NMR ($CDCl_3$): δ −380 (150 Hz). ^{15}N NMR ($CDCl_3$): δ 59.2 (5.5 Hz). ^{17}O NMR ($CDCl_3$): δ 1209 (370 Hz, V=O), 386 (1870 Hz, 3 V–O). $[\alpha]_D^{24}$ +89.7° ($c = 0.58$, C_3H_6O). EI–MS: *m/z* 321 $[M]^+$, 303 $[M-H_2O]^+$, 291 $[M-CH_2O]^+$, 273 (100%) $[M-H_2O-CH_2O]^+$. *Anal*. Calc. for $C_{14}H_{24}NO_4V$: C, 52.34; H, 7.53; N, 4.36. Found: C, 52.51; H, 7.75; N, 4.31%.

*2.2. (1′R,3S)-5-Aza-6′,6′-dimethyl-1-oxo-1-vanada-2,8,9-trioxabicyclo[3.3.3]undecane-3-spiro-2′-bicyclo[3.1.1]heptane (**3b**)*

Yield: 750 mg (78%), m.p. 248 °C. IR (cm^{-1}): 955 s ν(V=O), 630 m ν(V–O). ^{1}H NMR ($CDCl_3$): δ 0.94 (s, 3H, 13H or 14H), 1.24 (s, 3H, 13H or 14H), 1.57 (d, 10.5 Hz, 1H, 12H *anti* to C8), 1.78 (dm, 8.5 Hz, 1H, 10H), 1.89 (m, 1H, 9H), 1.91 (m, 1H, 10H), 1.96 (m, 1H, 7H), 2.04 (m, 1H, 11H), 2.10 (m, 1H, 11H), 2.14 (m, 1H, 12H syn to C-8), 3.01 (m, 1H, 4H or 6H), 3.05 (m, 1H, 6H or 4H), 3.07 (m, 1H, 4H or 6H), 3.08 (d, 13.5 Hz, 1H, 2H), 3.17 (m, 1H, 6H or 4H), 3.22 (d, 13.2 Hz, 1H, 2H), 4.56 (m, 4H, 3H and 5H). ^{13}C NMR ($CDCl_3$): δ 23.8 (C13 or C14), 24.8 (C10), 27.0 (C12), 27.3 (C13 or C14), 33.8 (C11), 38.2 (C8), 40.1 (C9), 54.9 (C7), 55.9 (C4 or C6), 56.8 (C4 or C6), 66.7 (C2), 73.6 (C3 or C5), 74.5 (C3 or C5), 89.7 (C1). ^{51}V NMR ($CDCl_3$): δ −400.4 (174 Hz). $[\alpha]_D^{24}$ +8.0° ($c = 0.25$, C_3H_6O). EI–MS: *m/z* 321 $[M]^+$, 303 $[M-H_2O]^+$, 291 $[M-CH_2O]^+$, 273 $[M-H_2O-CH_2O]^+$, 261 $[M-2CH_2O]^+$, 183 $[M-$pinanone$]^+$, 153 (100%) $[M-$pinanone$-H_2O]^+$. *Anal*. Calc. for $C_{14}H_{24}NO_4V$: C, 52.34; H, 7.53; N, 4.36. Found: C, 52.68; H, 7.39; N, 4.50%.

*2.3. (3S,2′S′,-5′R)-5-Aza-5′-methyl-2′-(1-methylethyl)-1-oxo-1-vanada-2,8,9-trioxabicyclo[3.3.3.]undecane-3-spiro-1′-cyclohexane (**3c**)*

Yield: 770 mg (76%), m.p. 200 °C. IR (cm^{-1}): 965 s ν(V=O), 635 m ν (V–O). ^{1}H NMR ($CDCl_3$): δ 0.76 (m, 1H, 9H), 0.79 (d, 6.0 Hz, 3H, 14H or 15H), 0.86 (d, 7.0 Hz, 3H, 12H), 0.88 (d, 6.2Hz, 3H, 14H or 15H), 1.04 (m, 1H, 7H), 1.06 (m, 1H, 11H), 1.46 (dquart., 12.4 Hz, 3.0 Hz, 1H, 8H), 1.55 (dt, 12.9 Hz, 2.7 Hz, 1H, 8H), 1.68 (m, 1H, 9H), 1.71 (m, 1H, 10H), 1.96 (m, 1H, 11H), 1.99 (m, 1H, 13H), 2.92 (d, 14.1 Hz, 1H, 2H), 3.00 (dd, 11.4 Hz, 5.7 Hz, 1H, 4H or 6H), 3.07 (td, 12.3 Hz, 3.6 Hz, 1H, 4H or 6H), 3.20 (td, 12.1 Hz, 3.2 Hz, 1H, 4H or 6H), 3.26 (m, 1H, 4H or 6H), 3.40 (d, 14.4 Hz, 1H, 2H), 4.49 (br, 1H, 3H‴ or 5H‴), 4.59 (td, 12.2 Hz, 4.2 Hz, 1H, 3H″ or 5H″), 4.60 (br, 1H, 3H‴ or 5H‴), 4.64 (td, 12.0 Hz, 3.9Hz, 1H, 3H″ or 5H″). ^{13}C NMR ($CDCl_3$): δ 18.1 (C14 or C15), 21.1 (C8), 22.2 (C14 or C15), 23.6 (C12), 26.6 (C13), 27.8 (C10), 34.3 (C9), 48.5 (C7), 51.9 (C11), 56.8 (C4 or C6), 59.3 (C4 or C6), 62.6 (C2), 74.3 (C3 or C5), 74.9 (C3 or C5), 95.1 (C1). ^{51}V ($CDCl_3$): δ −392

(181 Hz). $[\alpha]_D^{24}$ −83.3° ($c = 0.12$, C_3H_6O). EI–MS: m/z 337 $[M]^+$, 319 $[M-H_2O]^+$, 307 $[M-CH_2O]^+$, 289 $[M-H_2O-CH_2O]^+$, 277 $[M-2CH_2O]^+$, 183 $[M-$menthone$]^+$, 153 (100%) $[M-$menthone$-H_2O]^+$. *Anal*. Calc. for $C_{15}H_{28}NO_4V$: C, 53.40; H, 8.37; N, 4.15. Found: C, 53.66; H, 8.29; N, 4.03%.

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