Chinese Chemical Letters Vol. 10, No. 2, pp. 105–106, 1999

Synthesis of (4S)-4-Carboxyl-1-oxoperoxovanatranes

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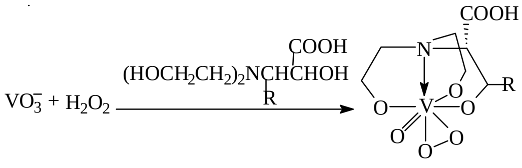
Abstract: (4S)-4-Carboxyl-l-oxoperoxovanatrane and (4S)-3-methyl-4-carboxyl-1-oxoperoxova-natrane were synthesized from the reaction of potassium vanadate, hydrogen peroxide with L-N, N-bis (2-hydroxyethyl) serine or L-N, N-bis (2-hydroxyethyl) threonine in water.

Keywords: (4S)-4-carboxyl-l-oxoperoxovanatranes, synthesis, chirality.

A number of vanadium haloperoxidase have been isolated from *marine algae* and *lichen’* and are thought to be involved in the production of a large number of halogenated organics *in vivo*[2]. The active site is shown to consist of an oxovanadium (V) with N/O donors[3-5]. Some vanatrane compounds (2.8.9-trioxa-5-aza-l-vanabicyclo [3.3.3] un-decanes) have been characterized as functional model from the vanadium haloperoxidases enzymes[6]. In fact, many classes of metalatrane compounds have been synthesized and studied because of their specific structure and biological activity[7]. Recently, two classes of chiral metatrane compounds, (4S)-4-carboxyl-l-alkysilatranes[8] and (4S)-4-carboxyl-l-hydroxylgerma-tranes[9], have been synthesized from the reaction of alkysilane or germanium dioxide with the chiral ligand L-N, N-bis (2-hydroxyethyl) serine or L-N, N-bis (2-hydroxyethyl) threonine respectively. In order to investigate the effect of the presence of 4-carboxyl group and chirality of the molecules on the biochemical function of vanatranes, and to compare with silatranes and germatranes, we accomplish the synthesis of (4S)-4-carboxyl-l-oxoperoxovanatrane **1** and (4S)-3-methyl-4-carboxyl-l-oxopero-xovantrane **2** from the reaction of potassium vanadate, hydrogen peroxide with L-N, N-bis (2-hydroxyethyl) serine or L-N, N-bis (2-hydroxyethyl) threonines in water, repectively.



1.R=H; **2.**R=Me

Potassium vanadate (5 mmol) in 20 mL of H_2O was stirred at 0℃. 2 mL of 30% aqueous hydrogen peroxide was added, and then the ligand (5 mmol) in 20 mL of water was added dropwise. Precipitate formed almost immediately upon addition of the ligand. The solution was stirred for 6 h, after which the red-orange powder was collected by filtration, washed once with cold ethanol, and air-dried. Yield 45-53%[10].

The carboxyl oxoperoxovanatranes were characterized by elemental analysis, EI-MS, ^{1}HNMR and IR spectra. The compounds are soluble in water, ethanol, and insoluble benzene, ether.

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10. **1** $[a]^{26}_{D}$=-50.6 (c=11.3×10^{-3}g/ml.H_2O).mp.131-132℃ (dec); EI-MS (m/z (%)) 289 (M^+, 12.1), 257 ($[M-O_2]^+$, 100) 245 ([M-CO_2], 41.3) 244 ($[M-COOH]^+$16.5) 213 ($[M-O_2-CO_2]^+$, 80.6); ^{1}HNMR (D_2O, ppm) 2.66-3.16 (4H, m, NCH_2×2) 3.35~3.78 (7H, m, NCH, OCH_2×3); IR (cm^{-1}, KBr) 3430 s (O-H), 1726 s, 1635 m (C=O) 1380 s (V=O) 950 (V-O_2) 571w (V-N).2 $[a]^{26}_{D}$= -41.0 (c=9.5×10^{-3}g/ml.H_2O).mp.127-128℃ (dec); EI-MS (m/z (%)) 303 (M^+, 9.4), 271 ($[M-O_2]^+$, 100), 259 ([M-CO_2], 60.3) 227 ([M-O_2-CO_2], 71.5); ^{1}HNMR (D_2O, ppm) 1.38 (3H, dCH_3) 2.65-3.16 (4H, m, NCH_2×2)3.28~3.80 (6H, m, NCH, OCH_2×2, OCH); IR (cm^{-1}, KBr) 3402 s (O-H), 1628 m, C=O), 1382 s (V=O), 953 s (O-O), 926 s (V-O_2), 568 w (V-N).

Received 28 July 1998