

Ozonolysis of 2-Methylthio-3-methyl-2-butene on Polyethylene: A New Access to Tetramethyl-1,2,4-Trioxolane

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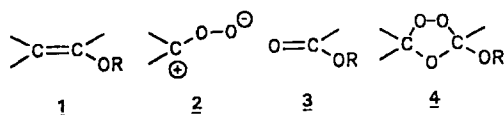
Received December 7, 1996

Vinyl ethers (**1**) are known to undergo selective cleavage with ozone to give fragments of types **2** and **3**.¹ Since esters (**3**) are poor dipolarophiles, [3+2]-cycloadditions between carbonyl oxides (**2**) and esters (**3**) to give alkoxy-substituted ozonides (**4**) are disfavored and, hence, such ozonides are formed in low yields or not at all, depending on the nature of the substituents. A case in point is the ozonolysis of 2-methoxy-3-methyl-2-butene, which did not afford the corresponding ozonide 3-methoxy-3,5,5-trimethyltrioxolane even upon ozonolysis on polyethylene, which is usually very conducive to ozonide formation.²

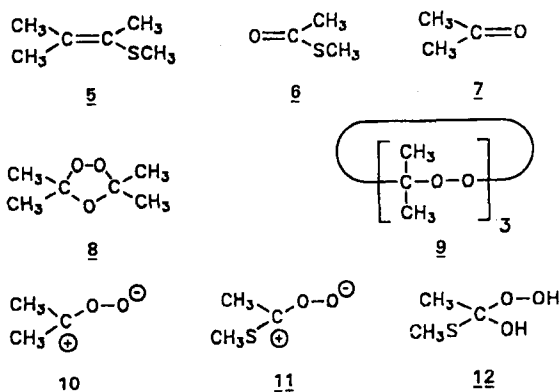
In connection with our work about ozonolysis reactions of vinyl ethers,² we became interested in the behavior of related vinyl sulfides towards ozone. To our knowledge, there is no report in the literature about the successful preparation of an ozonide of a vinyl sulfide, *i.e.* of an alkylthio-substituted ozonide. Instead, in the rare cases where vinyl sulfides have been ozonized, the corresponding thioester-fragments and/or abnormal, *i.e.* non-Criegee-type products have been found.³⁻⁵ In the present paper we report results of the ozonolysis of 2-methylthio-3-methyl-2-butene (**5**).

Ozonolysis of **5** on polyethylene at $-75\text{ }^{\circ}\text{C}$ afforded a mixture of compound **6** (54%), **7** (7%), **8** (11%), **9** (8%) and acetic acid (20%) in the relative proportions given in brackets, as determined by ^1H NMR spectroscopy. From such mixtures, ozonide **8** has been isolated in a yield of 7% by preparative gas chromatography.

The nature of the products indicates, that substrate **5** has



Formula 1.



Formula 2.

been cleaved by ozone into two directions, *viz.* into fragments **6** and **10** on one hand, and into **7** and **11** on the other hand. Apparently, the thioester **6** does not undergo [3+2]-cycloadditions with carbonyl oxides **10** or **11**. Instead, carbonyl oxide **10** reacts partly with acetone (**7**) to give ozonide **8**. This is remarkable, since in the past all attempts at preparing ozonide **8** by ozonolysis of the parent olefin **2,3**-dimethyl-2-butene in solution were futile.^{6,7} In fact, ozonide **8** has thus far only been accessible in low yield by ozonolysis of this parent olefin on polyethylene.⁸ The ozonolysis of **5** opens, thus, a second access to **8**.

The formation of **9** is also readily understandable, *viz.* by cyclotrimerization of **10**. By contrast, we could not find any experimental evidence for the existence and the possible fate of carbonyl oxide **11**, though the occurrence of acetone (**7**) would invoke the formation of **11** in the ozonolysis reaction. A conceivable possibility is the reaction of **11** with inadvertently present water *via* **12** to give H_2O_2 , methanethiol and acetic acid. Yet, while acetic acid has indeed been found as a reaction product, we have no evidence for the occurrence of methanethiol.

Experimental Part

Ozonolysis of **5** on polyethylene⁹

A solution of 893 mg (7.7 mmol) of **5** in 120 mL of diethyl ether was combined with 65 g of powdered polyethylene (particle size $\leq 20\text{ }\mu\text{m}$) and the slurry was stirred for ca. 20 min at room temperature. The solvent was evaporated at room temperature and reduced pressure, and the loaded polyethylene was treated with ozone at $-75\text{ }^{\circ}\text{C}$ for 8 hours and then flushed with nitrogen. The products were removed from polyethylene by evaporation at room temperature and 10^{-2} Torr, and they were collected in a trap kept at $-78\text{ }^{\circ}\text{C}$ to give 664 mg of a liquid crude product. ^1H NMR analysis (CDCl_3 , TMS) of the crude product showed the presence of **6** (54%; $\delta=2.30, 2.34$), **7** (7%; $\delta=2.17$), **8** (11%; $\delta=1.47$) and of acetic acid (20%; $\delta=2.10$). The structural assignments were confirmed by GC analysis (Shimadzu GC 6A; glass column $0.3\times 500\text{ cm}$, 5% Carbowax 20 in Chromosorb G; $60\text{ }^{\circ}\text{C}$ to $180\text{ }^{\circ}\text{C}$ at $4\text{ }^{\circ}\text{C}/\text{min}$) by coinjection of authentic samples to give the following retention times: **6** (9.59 min), **7** (4.65 min), **8** (6.97 min), acetic acid (13.15 min).

Isolation of **8.** The above crude product (530 mg) was separated by preparative gas chromatography (Perkin Elmer F-21; glass column $0.7\times 540\text{ cm}$, 5% methylsilicone on Chromosorb G; $80\text{ }^{\circ}\text{C}$) to give 71 mg (7%) of **8**. It was characterized by comparison of its ^1H NMR- ($\delta=1.47$, s; CDCl_3 , TMS), ^{13}C NMR- ($\delta=24.64$, q, 108.60, s; CDCl_3 ,

TMS) and EI MS data ($m/e=132$; M^+) with those of an authentic sample.

Isolation of 9. After evacuation of the loaded polyethylene was completed, the polyethylene was extracted with diethyl ether and the extract was concentrated at room temperature and reduced pressure. From the remaining solid residue (160 mg), one could isolate 51 mg (3%) of **9** by flash chromatography (15 g of silica gel; *n*-pentane/diethyl ether=10:1). Compound **9** was identified on the basis of its ^1H NMR ($\delta=1.46$, s; CDCl_3 , TMS) and ^{13}C NMR data ($\delta=21.30$, 107.47; CDCl_3 , TMS) with those reported.¹⁰

Acknowledgment. This work was supported by the Catholic University Research Fund, 1996.

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The Crystal Structure of Diammonium (Nitrilotriacetato)dioxovanadate (V)

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Received February 5, 1997

With the recent discoveries of the first two naturally occurring vanadium-containing enzymes, the bromoperoxidase and nitrogenase, the coordination chemistry and reactivity of vanadium is receiving renewed attention.¹ Of various ligands, many carboxylates are known to form anhydrides with vanadate in solution, when they have additional hydroxyl or amine groups available for chelation. Oxalate²⁻⁴ gives the simple mono- and bis-oxalato octahedral complexes, presumably with *cis*-VO₂ species. Also aminopolycarboxylate such as ethylenediaminetetraacetate (EDTA) forms similar octahedral complex having *cis*-VO₂ species.⁵⁻⁸ However, α -hydroxycarboxylates such as lactate, glycerate etc. form a variety of derivatives, including simple esters, chelates having trigonal bipyramidal coordination, and two binuclear complexes with mixed coordination.^{3,9,10}

But X-ray diffraction studies of vanadium (V) complexes are not much known yet. Only crystal structures of vanadium (V) complexes with oxalate^{11,12} and EDTA ligands^{13,14} have been determined. These complexes are confirmed to have a *cis*-VO₂ core, in which the anion has irregular octahedral geometry with two double-bonded oxygen atoms. In vanadium (V) complexes of oxalate^{11,12} it is known that the V-O (oxalate) bonds *trans* to V=O are longer than those *cis* to V=O.

In this paper, we report the synthesis of a new vanadium (V) complex, diammonium (nitrilotriacetato)dioxovanadate (V) ((NH₄)₂[VO₂NTA]), as well as its crystal structure determined by X-ray crystallography.

Experimental

Materials. All reagent grade chemicals were used without further purification. Ammonium metavanadate (NH₄VO₃), nitrilotriacetic acid (H₃NTA) and 25% ammonia water were purchased from Aldrich Chemical Company.

Preparation of vanadium(V) complex. The reaction of NH₄VO₃ (0.02 mole, 2.34 g) with H₃NTA (0.02 mole 3.82 g) and 25% ammonia water (0.02 mole, 1.3 mL) in 100 mL water produced yellow solution which was concentrated by passing a stream of dry air at room temperature for 2 days. The pale yellow crystals were formed and then filtered. The complexes were recrystallized from water. The yield was 1.95 g (63.1%). The single crystals were obtained by evaporating the aqueous solution of the complex. The chemical formula, VN₃O₈C₆H₁₄, of the complex was obtained from the elemental analysis. Analytical data (%) are in the range of good agreement (calculated; C 23.46, H 4.59, N 13.68, found; C 23.34 H 4.68 N 13.83).

X-ray measurements. Preliminary experiment and data collection for X-ray crystal structure determination were performed on a Enraf-Nonius CAD4/Turbo diffractometer using Mo K α radiation ($\lambda=0.71069$ Å). A small single crystal, 0.5×0.5×0.5 mm, was cut from a larger one and glued to a glass fiber with an epoxy resin. 25 reflections in diverse reciprocal space were centered by an automatic search program and used to obtain cell parameters. After the preliminary cell was confirmed, high-angle data