J. Am. Chem. Soc. 1989, 111, 3069-3070

considerable interest exists in the formation of polymers from other ring systems that have so far resisted polymerization.

Acknowledgment. We thank the U.S. Army Research Office for financial support and A. A. Dembek for obtaining high field ^{31}P and ^{1}H NMR spectra.

Oxidative Decarboxylation–Deoxygenation of 3-Hydroxycarboxylic Acids via Vanadium(V) Complexes: A New Route to Tri- and Tetrasubstituted Olefins

Ingrid K. Meier and Jeffrey Schwartz*

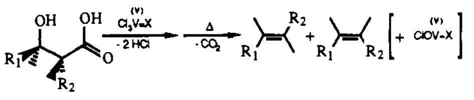
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

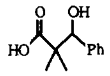
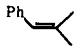
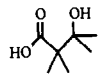
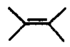
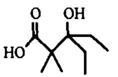
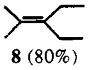
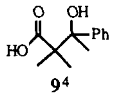
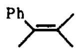
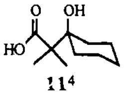
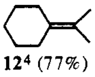
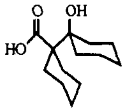
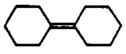
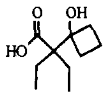
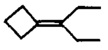
Received December 1, 1988

Oxidative decarboxylation of carboxylic acids is a "classical" procedure in synthetic organic chemistry which is well known in scope and mechanism. Surprisingly, whereas 2-hydroxycarboxylic acids have been studied in detail,[1] no similar investigations of 3-hydroxycarboxylic acids have appeared although these compounds are readily prepared by "aldol-type" condensation procedures.[2] We have now found that 3-hydroxycarboxylic acids readily undergo not only oxidative decarboxylation but also an unprecedented deoxygenation to yield olefins in the presence of an oxophilic metal species. This chemistry thus represents a direct route from aldol products to olefins.

Vanadium(V) is active for oxidative decarboxylation of 2-hydroxycarboxylic acids, but it is usually used in perchloric or sulfuric acid media, conditions which limit its scope of utility.[1] We find that readily available $VOCl_3$ is a convenient alternative source of reactive V(V) which can be used in the absence of added acid and which is comparable to aqueous V(V) compounds in its ability to oxidize carboxylic acids.[3] When $VOCl_3$ (0.5 mmol) was added to a suspension of 2,2-dimethyl-3-hydroxy-3-phenylpropanoic acid (**1**)[4] (0.5 mmol) in anhydrous chlorobenzene (5 mL) at room temperature, a homogeneous orange-red solution was obtained. Analysis by ^{1}H NMR and IR suggested the formation of a chelated vanadyl carboxylate.[5] When the solution of the adduct was heated to reflux, it became dark greenish-brown. After 30 min the reaction mixture was cooled, a few drops of water were added, and evaporative distillation yielded 2-methyl-1-phenyl-1-propene (**2**) (61%) and benzaldehyde (37%). No 2-methylpropanoic acid was produced; therefore, benzaldehyde is not formed by a "retro-aldol" reaction. Double bond isomerization products were observed in decarboxylation of several acids such as **3**, **7**, or **9** (see Table I). Such double bond isomerization could result from acid catalysis ($VOCl_3$ is a Lewis acid, and 2 equiv of HCl are generated overall in olefin formation). For example, treating 2-ethyl-3-hydroxy-2-methyl-3-phenylpropanoic acid (**3**) or the pure erythro diastereomer (**3a**) with $VOCl_3$ gave (*E*)- and (*Z*)-2-methyl-1-phenyl-1-butene (**4E** (26%) and **4Z** (14%)) as well as double bond isomers (27%); however, when **3a** was reacted with $VOCl_3$ in the presence of 1 equiv of Proton Sponge, only **4E** (27%) and **4Z** (20%) were formed. (Proton Sponge forms a complex with $VOCl_3$ which is only slightly soluble in chlorobenzene; longer reaction times are also needed to effect olefin synthesis when it is used.) Therefore, *E*/*Z* product formation, in contrast to double bond isomerization, need not be caused by proton catalysis.

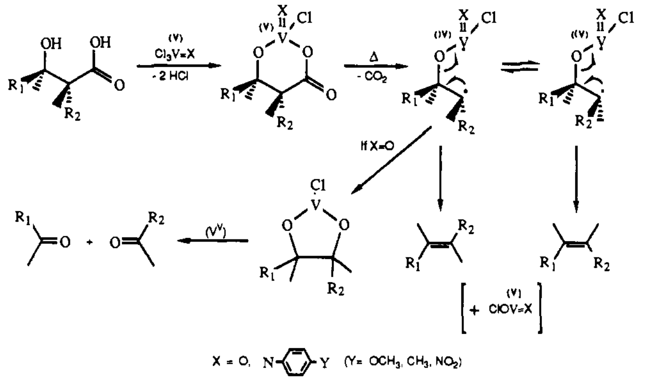
Table I



X	acid	conditions[a]	olefins[b]
O	 **1**[4]	+1 equiv of Proton Sponge 70 h	 **2** (73%)
$NC_6H_4CH_3$	**1**	24 h	**2** (72%)
$NC_6H_4CH_3$	 **5**[18]	19 h	 **6** (89%)
$NC_6H_4CH_3$	 **7**[19]	1,2,4-$C_6H_3Cl_3$; +1 equiv of Proton Sponge; 48 h, 132-4 °C	 **8** (80%)
$NC_6H_4CH_3$	 **9**[4]	+1 equiv of Proton Sponge; 49 h	 **10**[4] (>95%)
$NC_6H_4CH_3$	 **11**[4]	1,2,4-$C_6H_3Cl_3$; +1 equiv of Proton Sponge 70 h, 160 °C	 **12**[4] (77%)
$NC_6H_4CH_3$	 **13**[10b]	+1 equiv of Proton Sponge 68 h	 **14**[10b] (48%)[20]
$NC_6H_4CH_3$	 **15**[21]	+1 equiv of Proton Sponge 53 h	 **16**[21] (88%)

[a] Reactions were run in chlorobenzene unless otherwise stated. [b] Yields were determined by gas chromatography; all products were confirmed by GC/MS analysis comparison with actual samples.

Scheme I



---

(1) For examples of oxidative decarboxylation of 2-hydroxycarboxylic acids with V(V), see: (a) Jones, J. R.; Waters, W. A.; Littler, J. S. *J. Chem. Soc., London* **1961**, 630–2. (b) Mehrotra, R. N. *J. Chem. Soc. B* **1968**, 642–4. (c) Paul, S. D.; Pradhan, D. G. *Indian J. Chem.* **1972**, *10*, 562–3. (d) Virtanen, P. O. I.; Karppinen, S. *Finn. Chem. Lett.* **1984**, 34–7. (e) Kalidoss, P.; Srinivasan, V. S. *J. Chem. Soc., Dalton Trans.* **1984**, 2631–5. (f) Micera, G.; Deiana, S.; Dessi, A.; Pusino, A.; Gessa, C. *Inorg. Chim. Acta* **1986**, *120*, 49–51.

(2) For examples of aldol and "aldol-type" condensation reactions, see: (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. Stereoselective Aldol Condensations. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; John Wiley and Sons: New York, 1982; Vol. 13; pp 1–115. (b) Mukaiyama, T. *Org. React.* **1982**, *28*, 203–331. (c) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–81. (d) Heathcock, C. H.; Jarvi, E. T. *Tetrahedron Lett.* **1982**, *23*, 2825–8. (e) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *Tetrahedron Lett.* **1985**, *26*, 2125–8.

(3) Vanadium oxytrichloride (1.5 mmol) was added by syringe to a suspension of D-mandelic acid (1.5 mmol) in anhydrous chlorobenzene (5 mL), and the resultant solution was heated to reflux. Benzaldehyde was obtained (50%, 2 h).

(4) Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2000–6.

(5) 2,2-Dimethyl-3-hydroxy-3-phenylpropanoic acid (**1**): δ 4.68 (s, 1 H, C*H*Ph); vanadyl carboxylate, δ 7.36 (s, 1 H, C*H*Ph).

0002-7863/89/1511-3069$01.50/0

Imido derivatives of $VOCl_3$ were also found to be useful for oxidative decarboxylation. A series of such complexes, $Cl_3V{=}NC_6H_4X$ ($X = CH_3$,[8] NO_2,[9] or OCH_3[8]), was prepared. Qualitatively, rates for olefin formation from model hydroxy acid **3** were found to increase in the order $X = OCH_3 < CH_3 \leq NO_2$. Interestingly, the stereospecificity of olefination varied with the *opposite* trend. Thus for the *threo* diastereomer **3b**, the complex with $X = OCH_3$ gave an olefin ratio $E/Z = 7{:}1$ at short reaction times, but essentially no selectivity was observed for $X = CH_3$ or NO_2. The tolyl complex is particularly effective for preparing highly substituted olefins[10] (see Table I).

A mechanistic proposal which accounts for observed products and selectivities is shown in Scheme I. This involves formation of a carbon-centered radical via one-electron reduction of V(V) to V(IV) and subsequent decarboxylation.[11] Collapse of this radical would yield the olefin and generate a new V(V) oxo compound. Significantly, 3-hydroxy-3-methyl-2-phenylbutanoic acid (**18**)[12] gave both olefin **2** and benzaldehyde when treated with $VOCl_3$ in refluxing chlorobenzene. For benzaldehyde to be produced in this latter case not only must decarboxylation occur but also a new C–O bond must be formed. In support of a glycolate intermediate it was noted that benzaldehyde and 2-butanone were obtained from 2-ethyl-3-hydroxy-2-methyl-3-phenylpropanoic acid (**3**).[6] When imido complexes were used in place of $VOCl_3$, no cleavage occurred, and only olefins were formed.[13] If initial V–OC(O) homolysis were rate-determining, then an electron-withdrawing group on the aryl imido ligand (for example, NO_2) should accelerate the overall reaction relative to a donor ($X = OCH_3$).[14] The stereospecificity of the overall process would vary in the *opposite* direction: substituent groups which destabilize low-valent versus high-valent vanadyl should accelerate diradical collapse relative to stereochemical reorganization of the intermediate.[15] Cyclization of the 1,4-metallodiradical intermediate to vanadyl oxygen would give a glycolate which could cleave to give the carbonyl products observed.[16] We continue to investigate the mechanism and synthetic possibilities of this novel decarboxylation procedure.

Acknowledgment. We acknowledge support for this work provided by the National Institutes of Health and the National Science Foundation.

Supplementary Material Available: ^1H NMR and IR data for **1**, synthesis, separation, and spectral data (^1H NMR and ^{13}C NMR) for **3**, identification of erythro diastereomer of **3a**, synthesis and spectral data (mp, ^1H NMR, and ^{13}C NMR) for $Cl_3V{=}NC_6H_4NO_2$, **7**, and **15**, spectral data (^1H NMR, ^{13}C NMR, and HRMS) for **16**, and supplement to Table I (3 pages). Ordering information is given on any current masthead page.

---

[6] 2-Ethyl-3-hydroxy-2-methyl-3-phenylpropanoic acid (**3**) was prepared (43%) from 2-methylbutanoic acid and benzaldehyde. The diastereomers were separated by column chromatography (50:50:1 hexane/ether/acetic acid). The erythro diastereomer (**3a**)[7] was eluted first (mp 128.0–129.5 °C); the threo diastereomer (**3b**) was eluted next (mp 129.0–131.0 °C).

[7] The erythro diastereomer (**3a**) was identified by its conversion to (*E*)-2-methyl-1-phenyl-1-butene (**4E**) via anti elimination (Mulzer, J.; Pointner, A.; Chucholowski, A.; Bruntrup, G. *J. Chem. Soc., Chem. Commun.* **1979**, 52–4).

[8] Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408–16.

[9] $Cl_3V{=}NC_6H_4NO_2$ was prepared[8] from $VOCl_3$ and 4-nitrophenylisocyanate.

[10] Yields for tetrasubstituted olefins are at least comparable to those obtained using any of the three standard methods for making positionally defined olefins from 3-hydroxycarboxylic acids: For routes via β-lactones,[4] see also: (a) Noyce, D. S.; Banitt, E. H. *J. Org. Chem.* **1966**, *31*, 4043–7. (b) Krapcho, A. P.; Jahngen, E. G. E., Jr. *J. Org. Chem.* **1974**, *39*, 1650–3. (c) Schollkopf, U.; Hoppe, I. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 765. (d) Mageswaran, S.; Sultanbawa, M. U. S. *J. Chem. Soc., Perkin Trans. I* **1976**, 884–90. (e) Imai, T.; Nishida, S. *J. Org. Chem.* **1980**, *45*, 2354–9. For procedures via triphenylphosphine–diethylazodicarboxylate adducts[7] see, also: (f) Mulzer, J.; Lammer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 628–9. For a procedure via DMF–acetal, see: (g) Hara, S.; Taguchi, H.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1975**, 1545–8. For ethylpropylidenecyclobutane (**16**), for example, the β-lactone route gave only ~20% (by ^1H NMR) as a component of a complex mixture of products.

[11] Reduction of vanadium(V) to vanadium(IV) followed by rapid C–C bond fission to give the carbon-centered radical, $R_2\dot{C}(OH)$, is proposed as the rate-determining step in the oxidative decarboxylation of lactic, malic, and mandelic acids.[1a]

[12] Petrova, L. A.; Bel'tsova, N. N.; Remizov, A. L.; Vasil'eva, L. M. *J. General Chem. USSR* **1968**, *38*, 1654–7.

[13] Consistent with the notion that decarboxylation is a redox process, olefin synthesis from the imido complex adduct is slower than that from its vanadyl analogue.

[14] The arylimido group is likely a better electron donor than the oxo ligand. For a series of W analogues, see: Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547. Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826–2828.

[15] Similar diradicals have been proposed as intermediates in epoxide deoxygenation in which the stereospecificity of the process is believed to be related to oxidation of the metal in a 1,4-metallodiradical intermediate (Hayashi, Y.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 3473–6).

[16] Apparently only high-valent vanadium glycolates cleave. 2-Methyl-1-phenylpropane-1,2-diol (**17**)[17] reacted with $VOCl_3$, $VOCl_2$, and VCl_3, but benzaldehyde was formed in high yield (47%) only when $VOCl_3$ was used. Reaction with $VOCl_2$ gave rise to a lesser amount of benzaldehyde (3%), and VCl_3 gave no aldehyde; when 0.2 equiv of $VOCl_3$ was added to the VCl_3/diol solution, benzaldehyde was formed (90%) on reflux.

[17] Huffman, J. W.; Browder, L. E. *J. Org. Chem.* **1962**, *27*, 3208–3211.

[18] Cornforth, D. A.; Opara, A. E.; Read, G. *J. Chem. Soc. C* **1969**, 2799–2805.

[19] 2,2-Dimethyl-3-ethyl-3-hydroxypentanoic acid (**7**) was prepared from 2-methylpropanoic acid and 2-pentanone (mp 44.0–45.0 °C).

[20] The relatively low yield of this olefin may be related to conformational problems in the chelate intermediate. We thank a referee for bringing this to our attention.

[21] 2-(1-Hydroxycyclobutyl)-2-ethylbutanoic acid (**15**) was prepared from 2-ethylbutanoic acid and cyclobutanone (mp 68–9 °C).

Insertion of Oxygen into Vanadium–Carbon Bonds: Formation of $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ from $(\eta\text{-}C_5Me_5)_2V$ and O_2

Frank Bottomley,* C. Philippe Magill, and Peter S. White

Department of Chemistry, University of New Brunswick
Fredericton, New Brunswick E3B 5A3, Canada

Received December 5, 1988

It is well-known that oxidation of Cp_2V or $CpV(CO)_4$ ($Cp = \eta\text{-}C_5H_5$) with a large excess of dioxygen, followed by treatment with a source of chloride, gives high yields of $CpVCl_2(O)$.[1,2] The nature of the product of the initial oxidation is unknown. Recently similar reactions have been used to obtain $Cp^*VCl_2(O)$ from $Cp_2{}^*V$ or $Cp^*V(CO)_4$ ($Cp^* = \eta\text{-}C_5Me_5$).[3-5] We have shown that controlled oxidation of Cp_2V with a deficiency of a reagent containing oxygen gives $[CpV]_m(\mu_3\text{-}O)_n$ clusters and derivatives of these such as $Cp_{14}V_{16}O_{24}$.[6-8] We report here the remarkable controlled oxidation of $Cp_2{}^*V$ with O_2, giving $[\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$. *Three* oxygen atoms are inserted into adjacent V–C bonds in an all-cis configuration.

When $Cp_2{}^*V$ was incubated with O_2 (1:2 mol ratio) at −78 °C in hexane, the red solution initially became green, changing very rapidly to red-brown. After 1 h all the O_2 had been consumed. The red-brown solution was poured onto a column (1 × 40 cm glass beads, 120–200 mesh) and eluted with hexane. The first eluate was pale yellow; removal of the hexane under vacuum gave colorless platelets of $(C_5Me_5)_2$ (**1**).[9] A second eluate was ruby

---

[1] Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 1342.

[2] De Liefde Meijer, H. J.; Van Der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1418.

[3] Bottomley, F.; Sutin, L. *J. Chem. Soc., Chem. Commun.* **1987**, 1112.

[4] Herberhold, M.; Kremnitz, W.; Kuhnlein, M.; Ziegler, M. L.; Brunn, K. *Z. Naturforsch.* **1987**, *42B*, 1520.

[5] Herrmann, W. A.; Weichselbaumer, G.; Kneuper, H.-J. *J. Organomet. Chem.* **1987**, *319*, C21.

[6] Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 7226.

[7] Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651.

[8] Bottomley, F.; Drummond, D. F.; Paez, D. E.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1986**, 1752.

0002-7863/89/1511-3070$01.50/0