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Trimethyl Ester of Coenzyme PQQ in Redox Reactions with Transition Metals. An Efficient System for the Palladium-Catalyzed Ring-Opening Reaction of α,β-Epoxysilane

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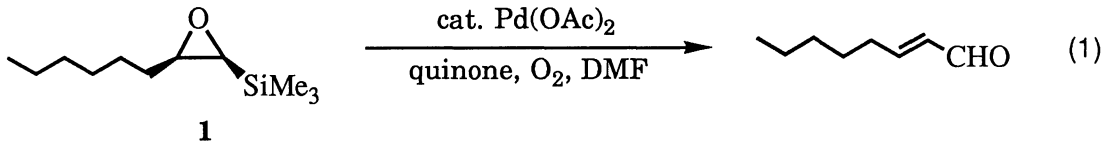
An efficient catalytic system for the palladium(II)-induced regioselective ring-opening oxidation reaction of α,β-epoxysilane was achieved by use of trimethyl ester of coenzyme PQQ under molecular oxygen. The redox cycle of the ester was performed with two different oxidation states of vanadium compounds, VCl_2 and $VO(OEt)_3$.

A facile reversible redox process of transition metals is required to realize an efficient catalytic oxidation reaction. Some methods have been developed to constitute such a system.[1] Coenzymes are expected to mediate transition metal induced oxidation reactions based on their smooth redox process. PQQ is a novel coenzyme involved in a variety of dehydrogenases.[2] The oxidative capability of PQQ depends on autocycling redox of the orthoquinone function under molecular oxygen. In a previous paper,[3] an efficient catalytic system has been achieved in the Wacker reaction by a combination of a palladium catalyst and trimethyl ester **2** of coenzyme PQQ. The generality of this system should be investigated in organic redox reactions.

The regioselective bond cleavage (β-cleavage) between β-carbon and oxygen of α,β-epoxysilanes is performed on treatment with transition metals such as palladium[4] and molybdenum salts,[5] which is in contrast to the normal α-cleavage with nucleophiles or electrophiles.[6] The β-cleavage reaction provides a useful method to generate transition metal enolates. A catalytic reaction has been tried in the palladium(II)-induced oxidation to α,β-unsaturated carbonyl compounds via palladium enolates. Silver oxide is found to regenerate an active palladium(II) species, but not so efficiently. Use of copper salt as a cooxidant leads to the predominant formation of byproducts. We herein report a palladium-catalyzed β-cleavage reaction that is effectively mediated by the quinone **2**.

Some quinones were examined on their efficiency in the palladium-catalyzed oxidation reaction of (*Z*)-1-trimethylsilyl-1-octene oxide (**1**, Eq. 1). The α,β-epoxysilane **1** (1 equiv.) was treated with a catalytic amount of palladium(II) acetate (0.1 equiv.) and the quinone **2** (0.1 equiv.) in anhydrous DMF under molecular oxygen at 70 °C for 7 h to give (*E*)-2-octenal stereoselectively in a good yield. Palladium(II) acetate was superior to palladium(II) chloride. Such an efficiency was not observed with methyl substituent in place of methoxycarbonyl one at 7-position. Other quinones including ortho- and para-derivatives gave poor results as shown below. With 1,7- or 1,10-phenanthrolinequinone, the ring-opening oxidation reaction was suppressed under the present conditions, presumably due to coordination[7] of the pyridine moiety to palladium species, interfering the redox interaction with the quinone function. These results suggest that the turnover of the catalyst depends on not only the nuclei structure but also the substituent of quinones.



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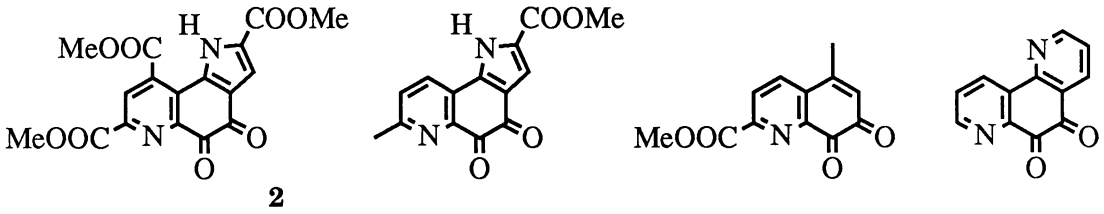


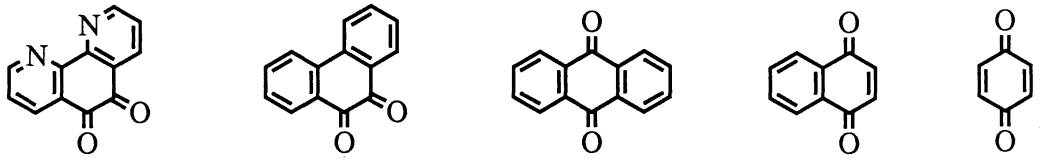
2

62%
21% ($PdCl_2$)

26%

21%

10%



trace

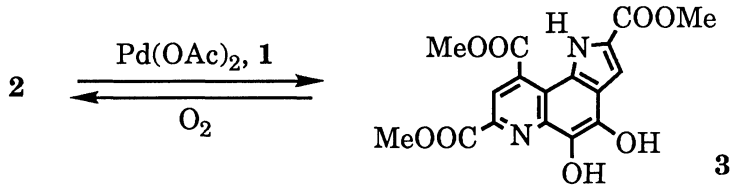
9%

23%

19%

19%

The redox process was monitored by UV-VIS spectra of **2** as shown in Fig.1. Treatment of a solution of **2** and palladium(II) acetate in DMF with **1** led to appearance of a new absorption maximum at 330 nm. It is attributed to the reduced quinol derivative **3** by comparison with the spectrum of its authentic sample. A large spectral shift was not detected in the presence of palladium salt. Reoxidation to **3** was easily performed only by bubbling molecular oxygen through the resulting mixture. This process was facilitated by a palladium salt present in the mixture.



3

The reduced palladium species which is generated in situ seems to undergo the facile reoxidation in the coordination sphere with **2**. Thus obtained quinol **3** is considered to be reoxidized to **2** with molecular oxygen. The complexation with **2** is proposed by analysis of cyclic voltammetry.[3] The present system is general and

versatile to achieve an efficient catalytic oxidation reaction, which is based on autocycling redox of **2** under molecular oxygen.

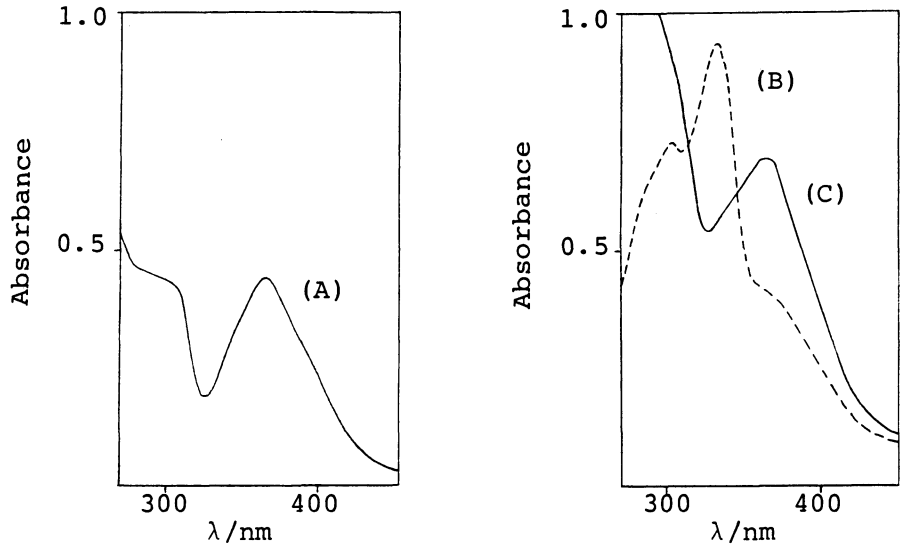


Fig. 1. UV-VIS spectra in the redox process of **2** with palladium(II) acetate. (A) The spectrum of **2** ([2] = 3 x 10^{-5} M) in the presence of $Pd(OAc)_2$ (1 equiv.) in DMF. (B) The spectrum after treatment with **1** (10 equiv.) at 70 °C for 5 h. (C) Molecular oxygen was bubbled through the solution obtained at the stage of (B) at room temperature for 8 h.

Reduction of **2** was performed with the low valent palladium species, but not with copper(I) chloride, iron(II) chloride, and $Mn(CO)_6$ under the similar conditions. Redox of PQQ is of importance to elucidate its function. Vanadium salts are known to play an important role in redox of naturally occurring compounds.[8] A strong reducing reagent, VCl_2,[9] was found to be effective for this reduction. The quinone **2** was converted to the corresponding quinol **3** on treatment with VCl_2 (10 equiv., 0.2 M) in acetonitrile-water (5:1 V/V) at room temperature for 15 h under argon. Bubbling molecular oxygen through the resulting solution at room temperature for 15 min led to the vanadium-assisted facile reoxidation to **2**. The oxidation of the independently prepared quinol **3** (8 x 10^{-3} M, acetonitrile) was also achieved by treatment with $VO(OEt)_3$ (1 equiv.), the oxovanadium compound in a high oxidation state,[10] at room temperature for 4 h under argon. Thus obtained quinone **2** was again reduced to **3** in one-pot reaction with 5 equiv. of VCl_2 (the resulting solution, acetonitrile-water 5:1 V/V; room temperature, 15 h, argon). These processes were followed by UV-VIS spectra as mentioned above.

$$\mathbf{2} \underset{VO(OEt)_3}{\overset{VCl_2}{\rightleftharpoons}} \mathbf{3}$$

The redox interaction of a palladium catalyst with the PQQ derivative has potential for synthetic use.[11] Further investigations of the redox process with transition metals including the mechanistic aspect are now in progress.

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