Heterogeneous Permanganate Oxidation of 1,5-Dienes: A Novel Synthesis of 5-Substituted Butanolides

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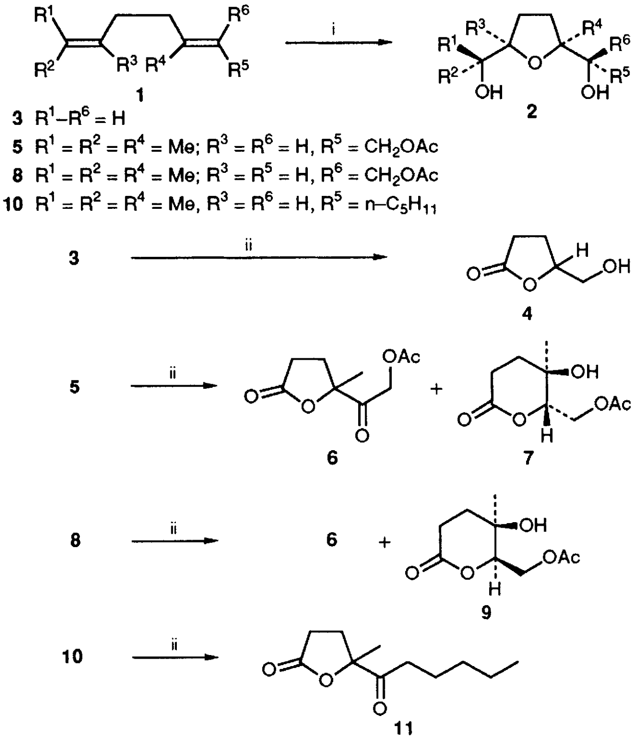
In the presence of a catalytic amount of water, 1,5-dienes undergo novel and unusual oxidation with potassium permanganate–copper sulfate in dichloromethane to give substituted butanolides in good yields under very mild conditions.

Klein and Rojahn[1] have reported that the oxidation of 1,5-dienes **1** with potassium permanganate under homogeneous conditions affords 2,5-bis(hydroxymethyl)tetrahydrofurans **2**, with relative stereochemistry as shown in Scheme 1. Independently, Walba[2] and Baldwin[3] confirmed the stereospecificity of this transformation. Recently, a high degree of enantioselectivity has been achieved in the homogeneous permanganate oxidation of 1,5-dienes to give 2,5-bis(hydroxymethyl)tetrahydrofurans.[4]

Although $KMnO_4$–$CuSO_4{\cdot}5H_2O$ has been used for the selective oxidation of secondary alcohols to ketones[5] and diols to lactones,[6] it has been reported to be inert towards alkenes.[7] We showed earlier that $KMnO_4$–$CuSO_4{\cdot}5H_2O$, in the presence of a catalytic amount of water and *tert*-butyl alcohol, can be effectively used for the direct conversion of alkenes to α-diketones and α-hydroxy ketones.[8] With this reagent system, a facile oxidative cyclization of γ-hydroxy alkenes to γ-lactones has also been achieved.[9] In the present study, heterogeneous permanganate oxidation of 1,5-dienes was found to lead to the formation of the corresponding butanolides in good yields (Scheme 1).†‡ The parent hexa-1,5-diene **3**, when treated with a well ground mixture of $KMnO_4$–$CuSO_4{\cdot}5H_2O$ and a catalytic amount of water in dichloromethane (6 h), gave the α-hydroxymethyl-γ-lactone **4**[10] in 20% yield.§ Under similar conditions, geranyl acetate **5** yielded the keto-γ-lactone **6** as the major product (62%) and the δ-lactone **7** as a minor product (8%) after 8 h, with the relative stereochemistry as indicated. On the other hand,



Scheme 1 *Reagents and conditions*: i, $KMnO_4$, homogeneous reaction; ii, $KMnO_4$–$CuSO_4{\cdot}5H_2O$, cat. H_2O, CH_2Cl_2

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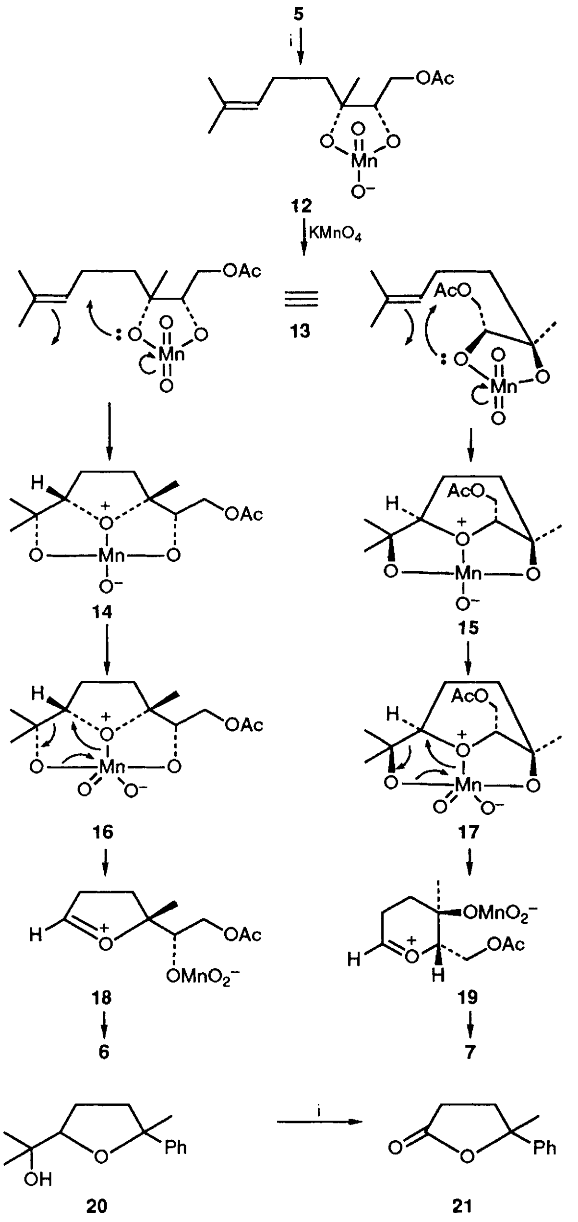
† In contrast to homogeneous permanganate oxidation of 1,5-dienes, we did not observe the formation of 2,5-bis(hydroxymethyl)tetrahydrofurans **2**.

‡ Typically, in the oxidation of geranyl acetate **5** with $KMnO_4$–$CuSO_4{\cdot}5H_2O$, to a stirred finely ground mixture $KMnO_4$ (8 g) and $CuSO_4{\cdot}5H_2O$ (4 g) to which water (400 μl) had been added, suspended in CH_2Cl_2 (15 ml), was added geranyl acetate **5** (2 mmol) in CH_2Cl_2 (5 ml). The mixture became warm (5 min) and then cooled. It was stirred for 8 h at room temperature (28 °C) and filtered through Celite, and the filtrant washed thoroughly with CH_2Cl_2. The solvent was evaporated off and the residue chromatographed on silica gel using ethyl acetate–light petroleum (b.p. 60–80 °C) (1 : 3) as eluent, furnishing the keto-γ-lactone **6** (62%) and δ-lactone **7** (8%).

All new compounds had satisfactory IR, NMR, mass spectral and analytical data; yields quoted in the text are isolated yields.

§ In the absence of water, the reaction does not take place.



Scheme 2 Possible mechanism; i, $KMnO_4$–$CuSO_4 \cdot 5H_2O$, cat. H_2O, CH_2Cl_2

neryl acetate **8** on treatment with this reagent system for 8 h afforded the keto-γ-lactone **6** as the major product (59%) along with the δ-lactone **9** (10%), which is a diastereoisomer of **7**. The diene **10**, under similar conditions, yielded the keto-γ-lactone **11** as the only product (47%) after 7 h.

Although several mechanisms have been postulated[2,3,11] for the homogeneous permanganate oxidation of 1,5-dienes, there is experimental evidence that this reaction takes place *via* the sequential oxidation of double bonds.[11] A plausible mechanism has been delineated by invoking Baldwin's[3] and Wolfe's[11] proposals for the formation of **6** (**5** → [**12**] → [**13**] → [**14**] → [**16**] → [**18**] → **6**) and **7** (**5** → [**12**] → [**13**] → [**15**] → [**17**] → [**19**] → **7**) in the heterogeneous permanganate oxidation of geranyl acetate **5** (Scheme 2). The possible involvement of hydroxymethyltetrahydrofuran derivative in this reaction was tested[12] by carrying out the reaction on compound **20**,[13] which underwent a facile oxidative cleavage to the corresponding lactone **21**[13] in good yield (72%).

Although the mechanism of this novel transformation is speculative at this stage, it is evident that the oxidation of 1,5-dienes with permanganate, under heterogeneous conditions to form 5-substituted butanolides, should be useful in organic synthesis.

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