

Oxidative Studies of Vicinal Diols, α -Hydroxyketones and α -Diketones Using Solid-Supported Potassium Permanganate on Silica Gel¹

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Foram investigadas as reações de clivagem oxidativas de dióis vicinais, α -hidroxicetonas e α -dicetonas com KMnO_4 adsorvido em sílica gel. Apenas os primeiros substratos sofreram reações nas condições empregadas. Os rendimentos obtidos são excelentes e a reação facilmente efetuada.

The oxidative cleavage of vicinal diols, α -hydroxyketones and α -diketones by silica gel-supported KMnO_4 reagent were studied. Only vic-diols were cleaved under the conditions employed. The reaction is easily performed and the yields are excellent.

Keywords: *diols cleavage, solid-supported reagent*

Introduction

There are a number of methods for oxidative cleavage of vicinal diols, such as $\text{NBS}/\text{Ph}_3\text{Bi}/\text{K}_2\text{CO}_3$ ². Reagents of tungsten³, iron⁴, vanadium and molybdenum⁵ have also been used for the same purpose. However, the most widely used are periodic acid^{6,7} and lead tetraacetate^{7,8}, which can be considered complementary methods, since the former is used mainly in aqueous medium and the latter in organic solvents.

A few years ago, we introduced the use of potassium permanganate supported on silica gel reagent⁹ as a convenient reagent to cleave carbon-carbon double bonds. In this paper we would like to present our results on the use KMnO_4 /silica gel to achieve *vic*-diol oxidative cleavage under very mild conditions and the attempts made to oxidize α -hydroxyketone and α -diketones.

The advantages of this method, according to our point of view, are: (a) the reaction occurs at room temperature and within a short reaction time, performed by a simple percolation of a solution of the diol through a short chromatographic column (1 h), except entry 7 (Table 1); (b) for

compounds leading to ketones (entries 2 and 4) the products are eluted with the solvent which makes its isolation exceedingly easy; and (c) the low cost of the reagent.

Our results are summarized in Table 1 and show that despite no attempt having been made to maximize yields, good to excellent yields of cleavage products were obtained.

Previous attempts to cleave benzopinacol (entry 7) with PCC by Cisneros and co-workers failed¹⁰. Using our methodology we had to pass the diol solution twice through the oxidant column, since after the first percolation we detected a large amount of starting material, which was quantitatively transformed into the product when passed through the column a second time.

When we tried to extend this methodology to the cleavage of α -hydroxyketones the main product obtained was the α -diketones and no further oxidation was observed. Using freshly purified α -diketones no oxidative cleavage was observed, and the starting material was recovered unreacted after being percolated through the column containing the oxidant, under similar conditions used in the cleavage of the vicinal diols.

Experimental Details

General

¹H NMR spectra were recorded on a Varian FT-80A or a Perkin-Elmer Hitachi R-24A spectrometer. Mass spectra were obtained on a Hewlett-Packard 5995 GC-MS with ionizing voltage of 70 eV. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 instrument. Melting points were determined on a Kofler apparatus and are uncorrected.

Preparation of silica gel/KMnO₄ reagent

Silica gel (15 g, 70-230 mesh) was added to 0.06 M of aqueous potassium permanganate (375 mL), and the resulting mixture evaporated in a rotary evaporator (65-75 °C) to give a free flowing solid. The reagent was dried further in an oil vacuum pump (0.5 mmHg) for two hours at 40-50 °C.

Cleavage of vicinal diols: a typical procedure. Valeric acid (12)

To 10.0 g of silica gel-supported KMnO₄ in a chromatographic column (25 mm i.d.) was added 1,2 hexanediol (11) (107 mg, 0.906 mmol) dissolved in methylene chloride (50 mL). After the solution was percolated more solvent (40 mL) was added and pressure was applied on top of the column. After evaporation of the solvent, 4.3 mg of the

starting material was recovered. Water was then added (150 mL) and eluted under pressure. The aqueous phase was acidified (H₂SO₄) and treated with solid (NaHSO₃), and extracted with ethyl ether (3 x 50 mL). After drying with anhydrous Na₂SO₄ the solvent was removed at reduced pressure in a rotary evaporator and then in an oil vacuum pump (0.5 mmHg), affording 12 (89 mg, 96% yield). The ¹H-NMR and infrared spectra were in agreement with the literature^{11,12}.

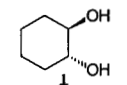
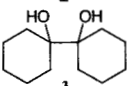

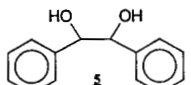
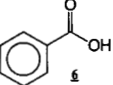


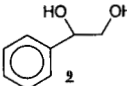
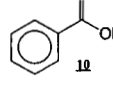
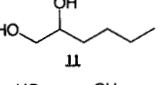
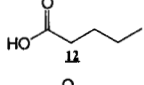
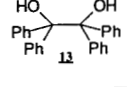

Acknowledgments

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Table 1. Diols cleavage by KMnO₄/silica gel.

entry product	compound	product ^a	yield, % ^b
1		HO ₂ C(CH ₂) ₄ CO ₂ H 2	96
2			81
3			93
4			78
5			65
6			96
7			95 ^c

^aThe reaction time for entries (1-6) was 1 h; ^bYields refer to isolated products; ^cThe solution containing the substrate had to be reintroduced in the column. Reaction time was 2 h.