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An efficient and selective method for the epoxidation of olefins using urea-hydrogen peroxide and methyltrioxorhenium (VII) (MTO) catalyst with heterocyclic aromatic amines

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Abstract

An improved method is demonstrated for the efficient and selective epoxidation of alkenes in the absence of water using 0.5 mol% methyltrioxorhenium (VII) (MTO) catalyst, urea-hydrogen peroxide (UHP) as the stoichiometric oxidant and a catalytic quantity of the heterocyclic aromatic amine base, pyrazole. This method gave conversions comparable to those using 0.5 mol% MTO, 30% aqueous H_2O_2 and pyridine (12 mol%) for a number of simple olefin substrates. A kinetic study was undertaken using *trans*-β-methylstyrene as substrate to compare the rate of this MTO catalytic epoxidation reaction with the MTO/H_2O_2 catalytic epoxidation under other conditions. It was found that the reaction rate profile observed for this epoxidation under our conditions mirrored that for the epoxidation reaction which used 0.5 mol% MTO, 30% aqueous H_2O_2 and pyridine (12 mol%).

Keywords: Methyltrioxorhenium (VII); Urea-hydrogen peroxide; Catalysis; Epoxidation

1. Introduction

The oxirane functional group is a common feature in a number of biologically active compounds, thus the development of more efficient and selective means of oxirane ring construction is very important [1]. In 1991 the group of Herrmann [2] showed that methyltrioxorhenium (VII) (MTO) acts as an efficient catalyst for olefin epoxidation when combined with H_2O_2. Later Sharpless and coworkers [3] demonstrated that catalytic quantities of pyridine could enhance both reaction rate and selectivity via a process of ligand acceleration on the part of pyridine. An important feature of this system was that aqueous hydrogen peroxide could be used as the stoichiometric oxidant. Further improvements have been made to this procedure using other heterocyclic amine derivatives (most notably: pyrazole and 3-cyanopyridine) in place of pyridine [4,5]. However, hydrolysis of the oxirane ring under these conditions is always a potential problem and indeed this has been observed as a competing side reaction in some cases under these conditions [4,5]. To circumvent such unwanted side reactions, urea-H_2O_2 (UHP), an anhydrous source of H_2O_2 has been employed and used in the place of aqueous H_2O_2. Adam and Mitchell [6] showed that a range of olefins could be epoxidised using a system consisting of MTO (1 mol%) and UHP, unfortunately reaction times generally of the order 18–37 h were required to obtain reasonably good conversions. Epoxide hydrolysis products were also observed in the case of some acid sensitive epoxides (for example, α-methylstyrene oxide and 1,1-diphenylethene oxide). Boehlow and Spilling [7] employed 5 mol% of MTO with UHP (2 and 3 equiv.) for the regio- and stereoselective epoxidation of a number of dienes and functionalised olefins. Recently, Omar Bouh and Espenson [8] reported successfully epoxidising some unsaturated fatty acids and simple non-functionalised olefins with MTO (1–3 mol%) supported on niobium (V) oxide. Owens

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and Abu-Omar [9,10] also investigated the epoxidation of simple olefins using 2 mol% MTO and UHP in the ionic liquid [emim]BF_4 and they reported high conversions for a range of di- and trisubstituted olefins including styrene, but obtained only a moderate conversion for the alphatic terminal olefin, dec-1-ene.

These reported methods all suffer the disadvantage that a significant quantity of the expensive epoxidation catalyst MTO (1–3 mol%) must be used along with special reaction conditions in some cases (for example, use of an ionic liquid or niobia support) to obtain good conversions of olefin substrate to epoxide. For this reason we decided to investigate the epoxidation of a number of non-functionalised and functionalised alkenes using only 0.5 mol% MTO and a catalytic quantity of pyridine and pyrazole in order to try improve the efficiency of this anhydrous method whilst maintaining its simplicity and selectivity.

2. Experimental

2.1. Starting materials

Methyltrioxorhenium (MTO) (Aldrich), urea-hydrogen peroxide (UHP) (Aldrich), pyrazole (Aldrich), 1-phenylcyclohexene (Aldrich and Lancaster), α-methylstyrene (Aldrich), *trans*-β-methylstyrene (Aldrich), cyclohexene (Aldrich), cyclooctene (Aldrich), *trans*-stilbene (Aldrich), styrene (Aldrich), 4-methylstyrene (Lancaster), *trans*-cinamyl alcohol (Aldrich) and dec-1-ene (Aldrich) were employed without further purification.

2.2. Catalytic epoxidation

In a typical experiment: CH_2Cl_2 (3 mL) was added along with MTO (3.4 mg, 0.014 mmol), pyrazole (0.022 g, 0.32 mmol) and UHP (0.508 g, 5.4 mmol) and the mixture stirred at room temperature. Shortly afterwards, *cis*-cyclooctene (0.35 mL, 2.7 mmol) was added to the yellow coloured reaction mixture and the mixture stirred for 2 h. CH_2Cl_2 (5 mL), H_2O (3 mL) and a small quantity of MnO_2 were added and the mixture agitated until there was no further oxygen evolution. The organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3×5 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and evaporation under reduced pressure afforded *cis*-cyclooctene oxide as a colourless gum (0.336 g, 96% pure as determined by GC analysis).

2.3. Kinetic studies

2.3.1. Exp. A

A 50 mL round bottom flask was charged with; dry CH_2Cl_2 (18 mL), MTO (19.94 mg, 0.08 mmol) and UHP (2.26 g, 24 mmol) and the mixture was stirred at room temperature under nitrogen. This was followed soon after by the addition of *trans*-β-methylstyrene (2.08 mL, 16 mmol) and stirring was continued at room temperature.

2.3.2. Exp. B

A 50 mL round bottom flask was charged with; dry CH_2Cl_2 (18 mL), MTO (19.94 mg, 0.08 mmol), UHP (2.26 g, 24 mmol) and dry pyridine (0.15 mL, 1.9 mmol) and the mixture was stirred at room temperature under nitrogen. This was followed soon after by the addition of *trans*-β-methylstyrene (2.08 mL, 16 mmol) and stirring was continued at room temperature.

2.3.3. Exp. C

A 50 mL round bottom flask was charged with; CH_2Cl_2 (18 mL), MTO (19.94 mg, 0.08 mmol), *trans*-β-methylstyrene (2.08 mL, 16 mmol) and dry pyridine (0.15 mL, 1.9 mmol) and the mixture was stirred at room temperature. This was followed soon after by the addition of 30% aqueous H_2O_2 (2.7 mL, 24 mmol) and stirring was continued at room temperature.

2.3.4. Exp. D

A 50 mL round bottom flask was charged with; CH_2Cl_2 (14 mL), MTO (15.9 mg, 0.064 mmol), UHP (1.81 g, 19.2 mmol) and pyrazole (0.102 g, 1.5 mmol) and the mixture was stirred at room temperature. This was followed soon after by the addition of *trans*-β-methylstyrene (1.66 mL, 12.8 mmol) and stirring was continued at room temperature.

In all cases an aliquot of the reaction mixture (1 mL) was removed from the reaction vessel on a hourly basis. A small quantity of MnO_2 was then added to each aliquot of reaction mixture and it was left stirring for 15 min, the mixture was then dried by adding anhydrous sodium sulphate and then stored in the freezer until analysed by GC. This analysis was done in triplicate.

2.4. Instrumentation and analysis

Gas chromatographic (GC) analysis of the products obtained from the epoxidation reaction were performed on a Hewlett Packard (HP) 6890 series instrument equipped with a flame ionisation detector (FID). The chromatograph was fitted with a cyclodex-B capillary column (J & W Scientific) (30 m × 250 μm × 0.25 μm) (Agilent 112-2532).

High performance liquid chromatographic (HPLC) analysis of *trans*-stilbene was performed on an Agilent 1100 series instrument fitted with an ultraviolet detector set to 254 nm. The mobile phase used consisted of *n*-hexane (Panreac): 2-propanol (Chromasolv Riedel-de Haen) (9:1) mixture with a flow rate of 0.5 mL/min. The column used was a Chiralcel OD-H (Daicel Chemical Industries) (0.46 cm × 25 cm) fitted with a guard column composed of the same stationary phase. In all cases, the olefin conversions were calculated by simply determining the ratio of the peak areas for the olefin substrate and the epoxide product. The reliability of this method was vindicated when it was shown that the

crude product mass determined after work-up for some selected reactions corresponded well with the predicted mass.

In the case of the epoxidation of styrene, α-methylstyrene and *trans*-stilbene the epoxide enantiomers were separated into distinct peaks on chromatographic analysis, therefore in determining the reaction conversion, the area of the epoxide peak was taken as the sum of the individual areas for the peaks of the epoxide enantiomers.

The ^{1}H NMR spectra were recorded using a Bruker AMX300 (300.13 MHz) instrument using $CDCl_3$ as solvent and TMS as internal standard.

3. Results and discussion

In our initial studies using this system [MTO (0.5 mol%) and pyridine (12 mol%)] only 1.5 equiv. of commercial UHP (this contains ca. 90% active H_2O_2 [11]) were used giving generally mediocre conversions for a number of common olefinic substrates [12]. The epoxidation conditions were subsequently optimised and improved results were thus obtained using 3 equiv. of UHP (Table 1). We observed that these reactions were generally fast and highly selective for the epoxide product. However, in some cases (for example, dec-1-ene and styrene) the conversions were low (Table 1).

In order to try to improve the efficiency of this epoxidation system we replaced pyridine with other heterocyclic amines, for example imidazole and pyrazole. The latter amine was selected on the basis of a literature precedent [4,5] which showed pyrazole to be superior to pyridine for the epoxidation of simple olefins. The results of this study demonstrated that under these new conditions the efficiency of the epoxidation reaction was superior to that which uses pyridine (Table 1).

Table 1
MTO catalysed UHP epoxidations with pyridine[a] and pyrazole[a]

Entry	Substrate	Amine	Time (h)	Conversion (%)
1	1-Phenylcyclohexene	Pyridine	3	69[b]
2	1-Phenylcyclohexene	Pyrazole	3	91[b]
3	α-Methylstyrene	Pyridine	6	72[b,c]
4	α-Methylstyrene	Pyrazole	4	93[b,c]
5	*trans*-β-methylstyrene	Pyridine	6	75[b]
6	*trans*-β-methylstyrene	Pyrazole	6	99[b]
7	Cyclohexene	Pyridine	6	99[b]
8	Cyclohexene	Pyrazole	5	96[b]
9	Cyclooctene	Pyridine	2	96[b]
10	Cyclooctene	Pyrazole	2	96[b]
11	Dec-1-ene	Pyridine	16	35[b]
12	Dec-1-ene	Pyrazole	16	91[b]
13	Styrene	Pyridine	16	39[b]
14	Styrene	Pyrazole	16	93[b]
15	4-Methylstyrene	Pyrazole	14	91[b]
16	*trans*-cinamyl alcohol	Pyridine	14	90[b]
17	*trans*-cinamyl alcohol	Pyrazole	16.5	91[b]
18	*trans*-stilbene	Pyridine	45	35[d]
19	*trans*-stilbene	Pyrazole	49	98[d]

[a] Reagents and conditions: MTO (0.5 mol%), UHP (2 equiv. for pyrazole catalysed reactions and 3 equiv. for pyridine catalysed reactions), amine (12 mol%), CH_2Cl_2, r.t.

[b] Determined by GC analysis.

[c] 3% diol was obtained in the pyridine catalysed reaction whilst 14% diol was obtained in the pyrazole catalysed reaction (this is based on the ratio of diol to epoxide present in the reaction mixture at the end of the reaction as determined by chromatographic analysis).

[d] Determined by HPLC analysis.

For example, conversions of over 90% were obtained for both dec-1-ene and styrene and in all but one case the selectivity was >99%. In the case of the epoxidation which afforded the very acid sensitive epoxide, α-methylstyrene oxide, a selectivity of 86% was obtained. The amount of diol side product (relative to epoxide) increased from 3 to 14% (Table 1) on switching from pyridine to pyrazole. The reaction time was subsequently lowered to 2 h and gratifyingly no diol side product was observed, however, the reaction conversion dropped to 68%. We also have investigated lower MTO catalyst loadings. An amount of 0.1 mol% MTO was employed with UHP (2 equiv.) and pyrazole (12 mol%) for the epoxidation of α-methylstyrene and *trans*-β-methylstyrene. However, conversions of only 36 and 47%, respectively, were obtained.

Preliminary studies were also conducted on the epoxidation of *trans*-β-methylstyrene using imidazole as amine additive with both 30% aqueous H_2O_2 and UHP as terminal oxidant. However, in both systems the conversions were found to be lower than those using pyridine or pyrazole [12]. As imidazole ($pK_a = 6.9$ [13]) is a more basic aromatic amine than either pyridine ($pK_a = 5.25$ [13]) or pyrazole ($pK_a = 2.5$ [14]) it is presumed that imidazole led to the decomposition of the MTO during the reaction.

A comparative study was next undertaken to investigate the reaction rates for the MTO catalysed epoxidation of *trans*-β-methylstyrene using four types of reaction conditions [Exp. A; MTO (0.5 mol%) and UHP (1.5 equiv), Exp. B; MTO (0.5 mol%), UHP (1.5 equiv.) and pyridine (12 mol%), Exp. C; MTO (0.5 mol%), 30% H_2O_2 (aq) (1.5 equiv.) and pyridine (12 mol%) and Exp. D; MTO (0.5 mol%), UHP (1.5 equiv.) and pyrazole (12 mol%)]. In all cases the concentration of substrate at the beginning of the reaction was 0.8 M. The reaction rate profiles for the first 3 h of each reaction are shown in Fig. 1.

It is obvious from this study that there is distinct reaction acceleration in the initial part of the epoxidation reaction (0–2 h) for both the pyridine and pyrazole catalysed reactions. This observation could be explained in three ways: (1) in the presence of pyridine or pyrazole the concentration of HOO^- will be greater thus inevitably leading to a greater concentration of the η^2-peroxo complexes [15], (2) pyridine and pyrazole accelerate the formation of the η^2-peroxo complexes [15], and (3) pyridine and pyrazole activate via complexation the η^2-peroxo complexes thus accelerating the epoxidation of olefins [15]. It is evident also that the MTO/UHP system employing pyrazole gives a reaction acceleration comparable to the Sharpless system (Exp. C). Lastly, it is important to consider that the epoxidation

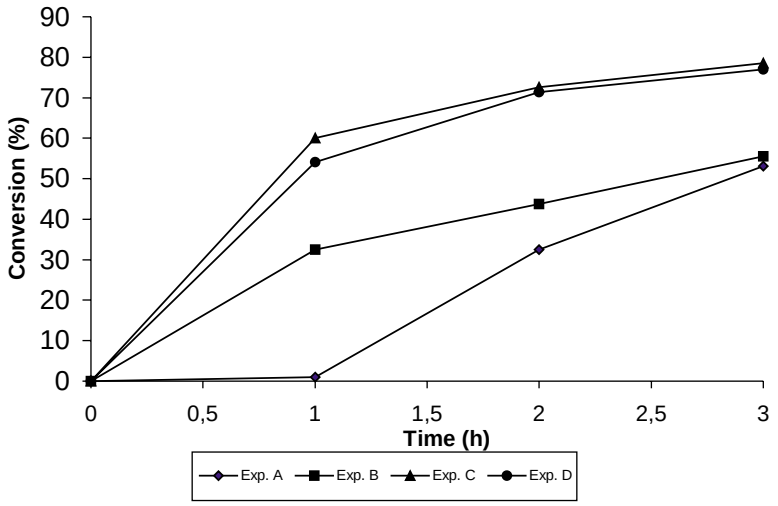

Fig. 1. Comparative study of the initial rates of reaction for the MTO catalysed epoxidation of *trans*-β-methylstyrene using: Exp. A; MTO (0.5 mol%) and UHP (1.5 equiv.), Exp. B; MTO (0.5 mol%), UHP (1.5 equiv.) and pyridine (12 mol%), Exp. C; MTO (0.5 mol%), 30% H_2O_2 (aq) (1.5 equiv.) and pyridine (12 mol%), Exp. D; MTO (0.5 mol%), UHP (1.5 equiv.) and pyrazole (12 mol%).

reaction in the absence of amine additive (Exp. A) is much slower in the beginning as it only commences ca. 1h after the last reagent is added. One possible reason for this could be in the absence of base the concentration of HOO^- will be lower and thus formation of η^2-peroxorhenium complexes slower. We are currently investigating other possible mechanisms, which could account for this lag period in the non-base catalysed MTO/UHP epoxidation reaction.

4. Conclusions

In conclusion, we have shown that MTO catalysed epoxidation of a range of simple olefins using UHP and a catalytic quantity of pyrazole is a highly efficient and generally selective method for the synthesis of epoxides which competes very well with the aqueous biphasic system developed by Sharpless and coworkers [3] and at the same time represents an improvement on previous MTO/UHP epoxidation methods.

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