



Original Research article

Epoxidation of Norbornene in the Presence of Oxidizing Agents

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ARTICLE INFORMATION

Received: 11 June 2017
Received in revised: 25 July 2017
Accepted: 15 August 2017
Available online: 25 August 2017

DOI:
10.22631/chemm.2017.94094.1004

KEYWORDS

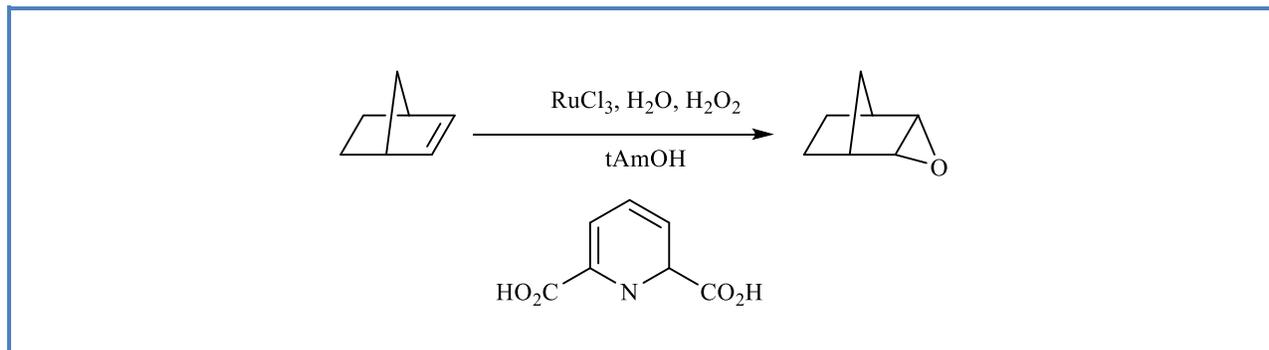
Dimethyldioxirane
Norbornen
Norbornadien
RuCl₃.H₂O.

ABSTRACT

Part1: epoxidation of norbornen and norbornadien in the presence of dimethyloxirane as reagent oxidant has been investigated.

Part 2: A general procedure for the epoxidation of norbornen using hydrogen peroxide as the oxidant in the presence of ruthenium trichloride has been investigated. norbornene gave the epoxides at room temperature in good to excellent yield. And epoxy norbornene identified by H-NMR, FT-IR, ¹³C-NMR method spectroscopics

Graphical Abstract



Introduction

Synthetic methodologies is one of the most important goals of current chemical research [1]. In the regard reactions should proceed with high atom-economy [2], thereby minimizing the cost of raw materials and of waste disposal. Although oxidation reactions constitute core technologies for converting bulk chemicals to useful products of a higher oxidation state, they are still among the more problematic processes. Even today, most of the known textbook oxidation methods lead to a significant. Amount of waste and therefore are unacceptable for industrial applications. Hence, there is a significant need for the development of cleaner and safer oxidation procedures. Obviously, molecular oxygen is the ideal oxidant for oxidation reactions [3]. However, the use of O₂ is sometimes difficult to control and in general only one oxygen atom from both oxygen atoms in O₂ is used productively for oxidation (50% atom efficiency) [4,5]. Thus, oxidation with molecular oxygen often require certain reducing agents to capture the second oxygen atom during the reaction. One of the few examples in which both oxygen atoms are used productively in oxidation reactions is the aerobic dihydroxylation of olefins, which we have developed some time ago [6]. Apart from molecular oxygen, hydrogen peroxide (H₂O₂) is a “green”, waste-avoiding oxidant [7,8]. It can oxidize organic compounds with an atom efficiency of 47% and generates among the different oxidation methods, the epoxidation of olefins is of major importance for organic synthesis. Nowadays, especially asymmetric epoxidation reactions are in the focus of methodological developments.

Epoxidation of norbornene in the presence of dimethyldioxirane.

General procedure for the preparation of epoxides 2 and 4:

A 0.075 M solution of dimethyldioxirane (80 mL, 6.0 mmol) was slowly added to a cooled (0°C) solution of norbornene 1 (2.0 mL) in CH₂Cl₂ (20 mL) under an argon atmosphere. The stirring was

continued at 0°C for 5 h. The solvents were evaporated under reduced pressure and the residue was chromatographed (flash silica gel: CH₂Cl₂: pet. ether, 2:1) to afford epoxide 2 (85% yield). Reaction pathways were shown in Figure 1.

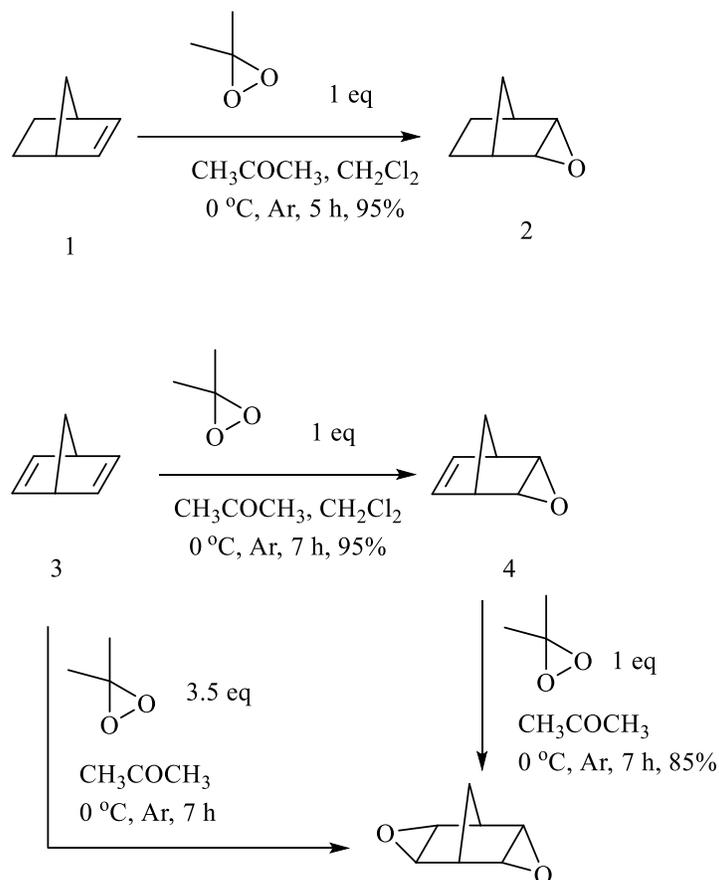


Figure 1. Epoxidation of norbornen

General procedure for epoxidation of norbornen by RuCl₃·xH₂O in *tert*-amyl alcohol

In a 25 mL Schlenk tube, substrate (0.5 mmol), catalyst solution (1 ml, 0.005 mmol, the catalyst solution was prepared by dissolving 10.4 mg, 0.05 mmol RuCl₃·xH₂O in *tert*-amyl alcohol to 10 mL) and pyridine-2,6-dicarboxylic acid (8.4 mg, 0.05 mmol) were dissolved in *tert*-amyl alcohol (8 mL). Then dodecane (100 L) was added as an internal GC standard. To this reaction mixture, a solution of hydrogen peroxide (1.67 mmol) in *tert*-amyl alcohol (1 mL) was added over a period of 12 h by a syringe pump. After 2 h of further stirring, a liquots were taken from the reaction mixture and subjected to GC analysis for determination of

yield and conversion data. For isolation of the products the reaction mixture was quenched with Na_2SO_3 solution (10 ml) and then extracted with dichloromethane (10 ml \times 2) and washed with water (20 mL). The combined organic layers were dried over MgSO_4 and evaporated to give the crude epoxides. The epoxides were purified by silicagel column chromatography (70–230 mesh), saturated with triethylamine (3%), and *n*-hexane/ethyl acetate (100:1) as the eluent. Reaction pathway were shown in Figure 2.

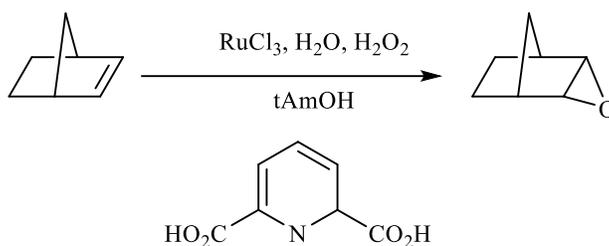


Figure 2. epoxidation of norbornene by $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in *tert*-amyl alcohol

Results and discussion

Epoxidation of norbornene by dimethyldioxirane (as an acetone solution) part one of our research. Dimethyldioxirane, either as a solution in acetone or generated in situ, is a well-known and powerful oxidizing agent. The dimethyldioxirane reagent is advantaged by efficiency, convenience of preparation and isolation, and on its performance under strictly neutral conditions. Oxidation of norbornene by chiral dioxiranes, generated in situ from a chiral ketone-catalyst and potassium monoperoxysulfate. Despite all its synthetic applications, little is known about the regioselectivity of dimethyldioxirane epoxidations, especially when two similar alkenes are present. To this end, some remarkable examples are the regioselective epoxidation of a disubstituted double bond over trisubstituted enol ether moiety, and the exclusive epoxidation (at an end cyclic double bond) of the pentafulvenes.

A great number of studies have been devoted to epoxy norbornene because these compounds which is a large-scale side-product of the coke and petroleum processing industries. In particular, derivative norbornene has found application for the industrial manufacture of various polymeric materials with valuable properties. Since this oxidation is usually carried out with peristatic, proxiphthalic and monoperoxymaleic acids, it was of interest to examine the behavior of such substrates towards dimethyldioxirane. Herein we report the epoxidation of norbornene by

epoxidation of norbornen in the presence of dimethyldioxirane gave only epoxy norbornen in 85% yield.

Spectra data of norbornene epoxid:

White crystals, ^1H NMR (400 MHz, 25 °C, CDCl_3): δ = 3.04 (s, 2H), 2.42 (s, 2H), 1.42–1.49 (m, 2H), 1.26–1.31 (m, 1H), 1.15–1.21 (m, 2H), 0.65–0.69 (m, 1H). ^{13}C NMR (400 MHz, 25°C, CDCl_3): δ = 51.4, 36.6, 26.2, 25.1. EIMS (70 eV): m/z = 110 (M^+ , 3), 109 (5), 95 (19), 92 (16), 91 (15), 82 (31), 81 (100), 79 (55), 55 (40), 54 (32), 41 (39), 39 (62), 27 (45).

Conclusion

Epoxidation of norbornenes by dimethyldioxirane (as an acetone solution) part one of the research in this paper. Dimethyldioxirane, either as a solution in acetone or generated in situ, is a well-known and powerful oxidizing agent. The dimethyldioxirane reagent is advantaged by efficiency, convenience of preparation and isolation, and on its performance. In summary, an easy and general epoxidation procedure of norbornen using hydrogen peroxide has been developed. The addition of pyridine-2,6-dicarboxylic acid as ligand to RuCl_3 led to a remarkable increase of activity and selectivity. For the first time epoxidation of norbornen with hydrogen peroxide in the presence of simple ruthenium salts are possible.

Norborne reacted in good to excellent yields (up to >99%) under mild reaction conditions (room temperature) The major advances of this method are simplicity, the cheapness of the ligand and the use of aqueous hydrogen peroxide as the oxidant.

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How to cite this manuscript: Hadi Jabbari. Epoxidation of Norbornene in the Presence of Oxidizing Agents. *Chemical Methodologies* 1(1), 2017, 68-73. [DOI: 10.22631/CHEMM.2017.94094.1004](https://doi.org/10.22631/CHEMM.2017.94094.1004).