

SHORT COMMUNICATION

A mild and effective method for the conversion of alkenes into alcohols in subcritical water

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Abstract: Alkenes were oxidized to alcohols in subcritical water. A number of alkenes were oxidized directly to their alcohols in excellent yields. The syntheses were performed in 215 cm³ stainless steel high pressure reactor at 120 °C in 150 cm³ water. The yields of alcohols increased with the nitrogen pressure.

Keywords: alkene, alcohol, subcritical water, oxidation.

INTRODUCTION

Several methods such as oxymercuration, hydroboration, treatment with water in the presence of an acid catalyst and addition of water to olefins in the presence of a transition metal catalyst as well as strong acid catalyzed reactions in subcritical water have been introduced in the literature for the hydration of alkenes.¹ Although the conversion of alkenes to alcohols have been known in subcritical media (Fig. 1),² many of the methods³ employ strong acids and metal catalysts which are not environmentally friendly. The use of subcritical water as a medium for chemical reactions has recently received a great deal of attention.^{4–5} In contrast to many other solvents, water not only provides a medium for solution chemistry but also often participates in chemical events. Water also offers practical advantages over organic solvents as it is inexpensive, readily available, non-toxic and non-flammable. A previous study,⁶ the oxidation of toluene to aromatic aldehydes with molecular oxygen in subcritical water was reported. In continuation of our recent work, oxidative coupling of thiols with molecular oxygen in subcritical water was performed⁷ and an alternative procedure for the conversion of alkenes into alcohols was reported.⁶

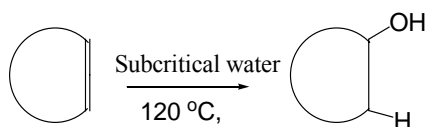


Fig. 1. Conversion of alkenes to alcohols.

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EXPERIMENTAL

IR spectra were recorded on a Win First Satellite[®] model spectrophotometer. ¹H-NMR spectra were obtained using a 400 MHz Bruker DPX[®] instrument.

General Procedure

The reactions were performed at 120 °C and in a 215 cm³ stainless steel pressure reactor⁵ equipped with a N₂ pressure gauge, safety valve, digital temperature reader, heater and magnetic stirrer. The pressure was kept at 50 bar with N₂. A glass vessel was inserted into the reactor to avoid the catalytic effect of steel and corrosion. The reactor was charged with alkene (1 g) and 150 cm³ H₂O. N₂ was supplied through a tube directly into the liquid phase. After completion of the reaction, the reactor mixture was cooled to room temperature and extracted with ethyl acetate (3×25 cm³). The combined organic extracts were dried (MgSO₄) and evaporated on a rotary evaporator under reduced pressure. Then the desired products were chromatographed over silica gel using ethyl acetate as the eluent. Evaporation of the solvent gave fairly pure alcohols, which were identified by IR and ¹H-NMR spectroscopy.


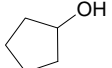

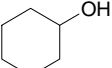

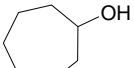

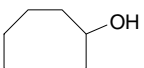

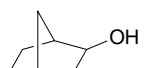
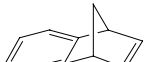
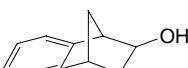
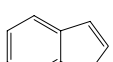
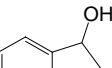
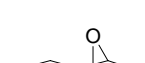
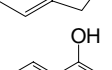
RESULTS AND DISCUSSION

In the present work, four monocyclic and four bicyclic olefins were converted into the corresponding alcohols in excellent yields. The reactions were performed at 120 °C under various pressures of nitrogen. The reactor was heated slightly before the reactions were commenced. Air oxygen and oxygen dissolved in water was removed from the reactor by bubbling nitrogen gas. Then, nitrogen gas was introduced into the reactor and the temperature was maintained at 120 °C. The reactions were monitored by TLC. In order to investigate effect of pressure on the yields, the reactions were carried out at different pressures. The yields were shown to depend on the nitrogen pressure. Reactions were performed at 20, 30, 40 and 50 bar of nitrogen. When the pressure was greater than 50 bar, the olefins polymerized. On the other hand, when the pressure was decreased below 20 bar, the reactions were incomplete. The ideal pressure was 50 bar of nitrogen. Similarly, different temperatures were examined. The best temperature was found to be 120 °C. All the products were characterized by their spectral data and comparison with reported data.⁸⁻¹⁰

As can be seen from Table I, the yields of alcohols from bicyclic olefins were slightly higher than from monocyclic olefins. The reactions times of the bicyclic olefins were shorter than those of the monocyclic olefins. It is assumed that these conversions proceeded *via* a radical mechanism, because the behavior of subcritical water as a radical oxidant in the presence of a metal catalyst has been known for a long time.² However, hitherto alkenes have not been converted to the corresponding alcohols in subcritical water without a metal catalyst. Oxabenzonorbornadiene (entry 8) was converted to 1-naphthol by the opening of the oxygen bridge, because the oxygen bridge is weaker than the methylene bridge. This result was to be expected.

The presented method is a simple, economic, environmentally friendly method for the transformation of olefins to alcohols.

Table I. Conversion of olefins into alcohols in subcritical water

Entry	Substrate	Product	τ / h	Yield / %			
				$p(\text{N}_2)$ / bar			
				20	30	40	50
1			8 ⁸	70	75	80	80
2			7 ⁸	75	80	85	85
3			8 ⁸	80	83	83	90
4			9 ⁸	78	85	82	85
5			4 ⁸	87	90	95	90
6			3 ⁹	73	78	80	85
7			3 ⁸	80	85	85	85
8			2 ¹⁰	75	80	83	85

Reactions conditions are exemplified in the general reaction procedure. Isolated yields obtained after chromatography. All products were characterized by ¹H-NMR and IR spectroscopic data and their physical data compared with literature data.

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ИЗВОД

ЈЕДНОСТАВАН И ЕФИКАСАН МЕТОД КОНВЕРЗИЈЕ АЛКЕНА
У АЛКОХОЛЕ У СУПКРИТИЧНОЈ ВОДИ

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У раду је приказан метод оксидације алкена до алкохола у супкритичној води. Већи број алкена је оксидован до оговарајућих алкохола са одличним приносом. Синтезе су обављене у реакторима од нерђајућег челика запремине од 215 cm³, који подноси високе притиске, при температури од 120 °C и запремини воде од 150 cm³. Принос алкохола растао је са притиском азота.

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