Monatshefte für Chemie 137, 1597–1600 (2006)
DOI 10.1007/s00706-006-0555-4

**Monatshefte für Chemie
Chemical Monthly**
Printed in Austria

Short Communication

Oxidation of Alcohols to Carbonyl Compounds, Benzylic Carbons to their Ketones, and Arenes to their Quinones with Molecular Oxygen in Subcritical Water

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Received May 25, 2006; accepted June 17, 2006

Summary. Molecular oxygen is used as an efficient oxidant for the conversion of alcohols into carbonyl compounds, benzylic carbons to their ketones, and arenes to their quinones in subcritical water in the absence of catalysts. The procedure utilizes water and does not require support materials and metal salts.

Keywords. Alcohols; Oxidation; Ketones; Subcritical water; Molecular oxygen.

Introduction

Oxidation of alcohols to carbonyl compounds is one of the most important reactions in organic chemistry [1]. Chromium(VI) reagents are widely used in organic chemistry for the oxidation of alcohols to carbonyl compounds [2]. The use of these oxidants as heterogeneous catalyst for various organic reactions is well known. It has been recently shown that alcohols are oxidized when treated under heterogeneous conditions, such as they occur with *Collins* reagent [3], pyridinium chlorochromate [4], pyridinium bromochromate [5], Cerium(III) bromate [6], or quinolinium fluorochromate [7]. There are several examples using organic molecules on solid support as oxidizing agents, such as silica gel or montmorillonite K10 [8]. However, several of the reported reagents suffer from disadvantages, such as instability, hygroscopicity, low selectivity, long reaction time, difficulty of

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preparation, and need for a large excess of the reagent. Thus, a mild, more selective, and inexpensive reagent is still in demand.

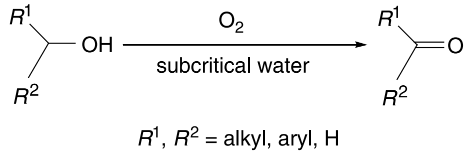
Since oxygen is highly soluble in subcritical water, it is one of the most attractive oxidants [9]. The increasing environmental concern surrounding the use of toxic and dangerous oxidants has impelled organic chemists to develop oxidation methodologies using molecular oxygen. In our previous study, we have reported the oxidation of toluenes to aromatic aldehydes with molecular oxygen in subcritical water [10]. In continuation of our recent work, oxidation of thiols to disulfides with molecular oxygen in subcritical water [11], we now wish to report conversion of alcohols to their corresponding carbonyl compounds without using metal salt catalysis in subcritical water.

Results and Discussion

In the present work, molecular oxygen is used to oxidize alcohols to their corresponding carbonyl compounds in subcritical water. The dramatic decrease in solvent viscosity and an increase in substrate solubility suggest that subcritical water may be useful as a replacement for environmentally unacceptable solvents for a number of organic reactions [12]. The oxidation of alcohols to carbonyl compounds in subcritical water was carried out as isothermal experiment at 120°C using different amounts of oxygen (Scheme 1). As shown in Table 1, all alcohols were converted to the corresponding carbonyl compounds, which were isolated in excellent yield. Because aliphatic and aromatic alcohols, benzylic corbons, and arenes were oxidized to their corresponding carbonyl drivatives in the absence of an organic solvent and metal salts/complexes, our method is indeed very green chemistry.

The amount of dissolved oxygen in water at atmospheric pressure was determined according to *Henry*'s Law [13] (at 25°C the solubility of O_2 is of 1.296×10^{-3} mol/kg H_2O). This value was used initially as shown in Table 1 as entry A. The amount of oxygen was regulated by the oxygen pressure. All oxidations were performed by adding 200 cm^3 of water, one equivalent of substrate, and two equivalents of oxygen. Since longer reaction times did not improve the yields, the time was different for all oxidations. On the other hand, when oxygen pressure was increased, the yields increased not beyond 20 bar. On the contrary, an increase in the amount of oxygen led to decomposition of the starting materials converting them into tars. All the products were characterized by their spectral data and comparison with reported data.

In conclusion, we developed a practical procedure for the oxidation of alcohols to their corresponding carbonyl compounds, in subcritical water with molecular



Scheme 1

Table 1. Oxidation of organic substrates with molecular oxygen in subcritical water (total pressure 50 bar, temperature 120°C)

Entry	Substrate	Product	Time/h [Ref.]	Yield/%[a] P_{O_2}/bar[b]				
				A[c]	5	10	15	20
1	*n*-Butanol	Butanal	2 [14]	75	77	80	90	90
2	*Iso*amylalcohol	3-Methylbutanal	3 [14]	73	77	80	85	85
3	1-Octanol	Octanal	2 [14]	70	80	92	95	95
4	Benzyl Alcohol	Benzaldehyde	1 [14]	85	85	93	95	95
5	2-Pentanol	2-Pentanone	2 [14]	90	92	95	95	95
6	Benzhydrol	Benzophenone	3 [14]	88	90	95	95	95
7	Cyclohexanol	Cyclohexanone	3 [14]	75	78	85	90	90
8	Cyclopentanol	Cyclopentanon	4 [14]	80	85	90	95	95
9	Cholesterol	3-Oxocholesterol	2 [14]	82	85	85	90	90
10	1-Menthol	1-Menthone	3 [14]	75	80	80	85	85
11	Indane	1-Indanone	2 [14]	72	75	80	85	85
12	Tetralin	Tetralone	1 [14]	70	73	75	75	80
13	Anthracene	9,10-Anthraquinone	1 [14]	80	85	88	90	90
14	Phenanthrene	Phenanthrene-9,10-quinone	1 [14]	72	75	85	85	85

[a] Yields refer either to 2,4-*DNP* derivatives identified by melting points or to isolated products for which melting points were taken directly; [b] double equivalents of molecular oxygen, 5 bar: 4.63×10^{-3} mol dm^{-3}, 10 bar: 9.26×10^{-3} mol dm^{-3}, 15 bar: 1.38×10^{-2} mol dm^{-3}, 20 bar: 1.85×10^{-2} mol dm^{-3}; [c] A: dissolved oxygen in water at atmospheric pressure: 1.26×10^{-3} mol dm^{-3}

oxygen in the absence of metal salt. This method is useful because it is simple, economic, and environmental.

Experimental

Mps were determined on an Electrothermal 9100® apparatus. IR spectra were recorded on a Win First Satellite® model spectrophotometer. ^{1}H NMR spectra were obtained using a 400 MHz Bruker DPX® instrument.

General Procedure

Oxidations were carried out at 120°C in a 215 cm^3 stainless steel pressure reactor equipped with N_2 and O_2 inlet, pressure gauge, safety valve, digital temperature reader, heater, and magnetic stirrer. The total pressure was kept at 50 bar by N_2. A glass vessel was inserted into the reactor to avoid corrosion. The reactor was charged with substrates and 200 cm^3 H_2O. All the valves of the reactor were tightly closed during preheating. N_2 was supplied through a tube into the liquid phase directly. Then the desired oxygen pressure was applied to the vessel through a stainless steel tube into the liquid phase directly. After completion of the reaction it was extracted with ether (3×20 cm^3). The combined organic layer was dried over $MgSO_4$ and evaporated on a rotary evaporator under reduced pressure. Then the product was chromatographed over silica gel using ethyl acetate:*n*-hexane (1:4) as the eluent to separate the product. After evaporation of the solvent, the fairly pure solid were crystallized. The liquid carbonyl compounds were derivatized with 2,4-dinitrophenylhydrazine. The melting points of solid compounds such as benzil, benzophenone, 3-oxocholestorol, 1-menthone, 1-indanone, tetralone, 10-anthraquinone, and phenanthrene-9,10-quinone were checked and all compounds were identified by spectral data like IR and ^{1}H NMR.

Acknowledgement

We are greatful to Mersin University Research Council and TUBITAK (The Scientific and Technical Council of Turkey) for supporting this work (Grant No: TBAG-2235).

References

[1] Degirmenbasi N, Ozgün B (2003) Monatsh Chem **134**: 1565
[2] Cainelli G, Cardillo G (1991) Chromium Oxidation in Organic Chemistry. Springer Verlag: Berlin
[3] Collins JC, Hess WW, Frank FJ (1968) Tetrahedron Lett **30**: 3363
[4] Corey EJ, Fleet GWJ (1973) Tetrahedron Lett **14**: 4499
[5] Loonker K, Sharma PK, Banerji KK (1997) J Chem Res (S) 194
[6] Shaabani A, Lee DG (2003) Synth Commun **33**: 1845
[7] Chaudhuri MK, Dehury KS, Dhar SS, Sinha BU (2004) Synth Commun **34**: 4077
[8] Hashemi MH, Ghazaanfari D, Akhbari M (2004) Monatsh Chem **135**: 797
[9] Holliday RH, Jong BYM, Kolis WJ (1998) J Supercrit Fluids **12**: 255
[10] Kayan B, Gizir AM, Ozen R, Kus NS (2005) Org Prep Proced Int **37**: 83
[11] Ozen R, Aydin F (2006) Monatsh Chem **137**: 307
[12] Gemperline PJ, Yang Y, Bian Z (2003) Anal Chem Acta **73**: 485
[13] Tromans D (2000) Ind Eng Chem Res **39**: 805
[14] Ride LD (1991–1992) CRC Handbook of Chemistry and Physics, 72nd ed. CRC Press Inc, Physical Constants of Organic Compounds

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Verleger: Springer-Verlag GmbH, Sachsenplatz 4–6, 1201 Wien, Austria. – Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, 1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, 1010 Wien, Austria. – Redaktion: Getreidemarkt 9/163-OC, 1060 Wien, Austria. – Satz und Umbruch: Thomson Press Ltd., Chennai, India. – Offsetdruck: Manz Crossmedia, 1051 Wien, Austria. – Verlagsort: Wien. – Herstellungsort: Wien. – Printed in Austria.