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Some Oxidation Reactions with Molecular Oxygen in Subcritical Water

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In this study, some alkyl arenes such as fluorene and ethyl benzene have been oxidized to the corresponding carbonyl compounds. 1,4-Diol and cyclic ethers give lactones and lactams, which are converted into corresponding imides under these conditions. This paper describes a simple and general procedure that can be used for the oxidative transformation of many organic functional groups.

Key Words: Oxidation, Subcritical water, Molecular oxygen.

INTRODUCTION

The transition-metal catalyzed oxidation of organic compounds with atom-efficient oxidants such as O_2 or H_2O_2 is rapidly gaining importance as a viable alternative way to achieve the environmentally hazardous, metal-promoted stoichiometric oxidation[1-11]. Recent studies have shown that transition metals in combination with various oxidizing agents convert a wide range of hydrocarbons to the corresponding oxidized products[12-18]. Although much research has been conducted, only a few studies have used O_2 as an oxidant[19-21]. One of the most attractive oxidants is molecular oxygen[22], since oxygen is highly soluble in subcritical water. This paper describes a simple and general procedure that can be used for the oxidative transformation of many organic functional groups by different amounts of molecular oxygen in subcritical water. The possibility of recycling water and control of the reaction product by temperature and pressure make this method clean, inexpensive and valuable from an environmental point of view.

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EXPERIMENTAL

All chemical reagents were commercially available. The substrates were purified (distilled or crystallized) before application in the reaction. ^{1}H NMR-^{13}C NMR spectra were recorded on a Bruker 400-100 MHz spectrometer and infrared spectra were obtained as films on NaCl plates for liquids and KBr pellets for solids on a Win First® Satellite Model infrared recording spectrophotometer. All column chromatography was performed on silica gel (60-mesh, Merck).

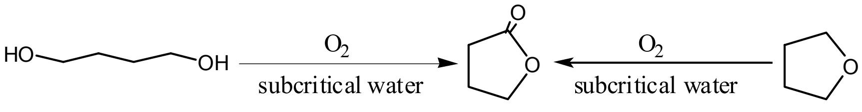
General procedure for the oxidation reaction: Oxidations were carried out at 110 °C in a 280 mL stainless steel reactor. A glass vessel was inserted into the reactor and the oxidation occurred without contact with the stainless steel reactor surface in order to avoid the catalytic effect of steel and corrosion. The catalyst (20 mg) and Al_2O_3 (20 mg), suspended in 50 mL water and substrate (5 mmol) were added to the stainless steel reactor. The reactor was heated to the desired temperature (110 °C) from the bottom on a hotplate and surrounded by heat-resistant material to prevent loss of heat and temperature. All the valves of the reactor were tightly closed during preheating. Then the desired oxygen pressure (10 bars) was applied to the vessel through a stainless steel tube into the liquid phase directly and the total reaction time was 4 h. After the reaction was completed, the mixture was cooled to room temperature and filtered and the residue was washed with $CHCl_3$ (3×40 mL). The solvents were then evaporated *in vacuo* and the products were purified by column chromatography on silica gel (60-mesh, Merck) with a 50 cm glass column and then analyzed by ^{1}H NMR spectroscopy as described above.

RESULTS AND DISCUSSION

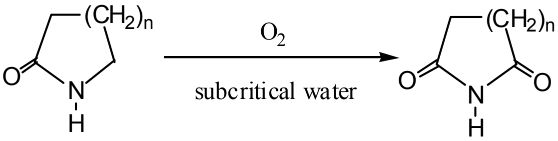
In this study we examined the oxidation of different substrates and different amounts of molecular oxygen, after 4 h reaction in subcritical water and the conversion of substrates was around 75-80 %. The reaction yields from these conversions have been calculated. The structures of all the products were identified by ^{1}H NMR analyses. After 4 h of reaction, conversion of the starting materials was 75-80 %. When the reactions were maintained for more than 4 h the product yields decreased due to decomposition continuing and the products began to decompose.

The amount of oxygen dissolved in water at 25 °C and at atmospheric pressure was determined according to Henry's Law[23] (1.296×10^{-3} mol O_2/kg of H_2O) and this value of oxygen was used initially as shown in Table-1 as A. The amount of oxygen was regulated by the oxygen pressure[23]. All oxidations were performed by adding 280 mL water, one molar equivalent of substrate and two molar equivalents of oxygen. On the other hand, when oxygen pressure was increased, the yields did increase beyond

20 bars. An increase in the amount of oxygen led to decomposition of the starting materials as they were converted to various uncharacterized tars (Table-1).

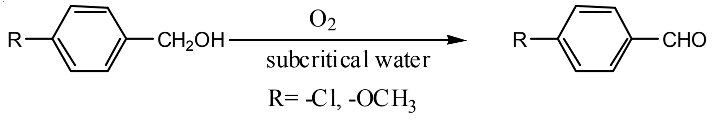


Scheme-I



Scheme-II

The oxidations were carried out at 110 °C in a 280 mL stainless steel reactor. As indicated in **Scheme-I**, 1,4-diol is easily and completely converted into lactones are important flavour and aroma constituents in many natural products, the procedures works well for the preparation of butyrolactones, under these conditions. 1,3 and 1,5-diols are converted into dialdehydes, attemps to obtain lactones failed. Cyclic ethers were also converted into lactons with oxygen in subcritical water.

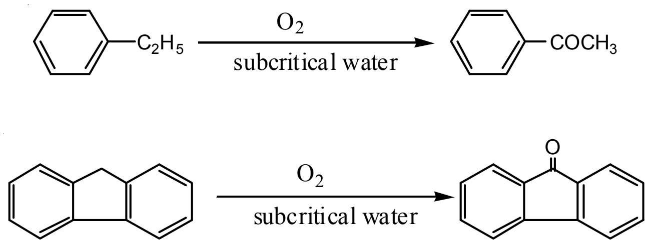


Scheme-III

Synthesis of cyclic imides are certainly important for both chemical industry and medicine. Some of these compound such as succinimide are used as growth stimulants for plants and as starting materials for the synthesis of heterocycles[24]. A cyclic imide moiety can be found in some natural product and in man-made compound. This method is a general as a variety of lactams were succeffully transformed into cyclic imides in subcritical water. This simple, economic, environmentally method is useful for the transformation of lactams to imides.

The preparation of aromatic aldehydes from the corresponding primary alcohols are diffucult have been easly achieved using molecular oxygen in subcritical water because aldehydes are so readly converted to carboxylic acids under oxidizing conditions.

This method is the mild condition of present reaction promise synthetic use for the oxidation of containing benzylic methylene groups to the corresponding carbonyl compounds (**Scheme-IV**).



Scheme-IV

TABLE-1
OXIDATION REACTION WITH O_2 IN SUBCRITICAL WATER (110 °C TEMPERATURE AND 10 BARS O_2 PRESSURE)

Substrate	Product	m.p. (°C)	b.p. (°C)	Yields (%) at O_2 pressure (bar)			
				5	10	15	20
1,4-butanediol	γ-Butyrolactone		206	48	50	60	63
Tetrahydrofuran	γ-Butyrolactone		206	65	68	70	75
Phthalan	Phthalide	73	290	60	65	67	70
Indan-1,3-dione	Isochroman-1,4-dione			53	60	63	68
p-Methoxybenzlalcohol	*p*-Methoxybenzaldehyde		238	60	62	65	70
p-Chlorobenzyl alcohol	*p*-Chlorobenzylaldehyde	48		50	55	59	65
Ethylbenzene	Acetophenone	21		60	63	72	80
Flourene	Flourenone	83		73	75	80	82
2-Pyrolidione	Succinimide	125		45	50	60	63
δ-Valerolactam	Glutarimide	156		45	45	50	60
ε-Caprolactam	Adipimide	170		35	40	42	55

Isolated yields: Products were identified from a comparison of physical and spectroscopic properties (melting points, mass spectra, infrared and NMR spectra) with literature values[25-28]. The oxidant was O_2. The conversions are obtained by GC analysis.

In conclusion, we performed a simple, clean and efficient catalytic oxidation procedure using molecular oxygen to obtain lactone, ketone, aldehydes and imides in high yields in subcritical water. ^1H, ^{13}C NMR and IR spectra of the products obtained are in good agreement with the expected structure.

ACKNOWLEDGEMENT

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REFERENCES

1. J.O. Edwards and R. Curci, in ed.: S.G. Kluwer, Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Dordrecht, Chapter 4, pp. 97-151 (1992).
2 R.A. Sheldon and J.K. Kochi, Metal-catalyzed oxidation of Organic Compounds, Academic Press, New York (1991).
3 B. Notari, *Catal. Today*, **18**, 163 (1993).
4 J.S. Reddy, R.U. Khire, P. Ratnasamy and R.B. Mitra, *Chem. Commun.*, 1234 (1992).
5 A. Butler, M.J. Clague and G.E. Meister, *Chem. Rev.*, **94**, 625 (1994).
6 S.E. Jacobson, R. Tang and F. Mares, *Chem. Commun.*, 888 (1978).
7 S. Campestrini and F.D. Furia, *J. Mol. Catal.*, **79**, 13 (1993).
8 W.A. Herrman, R.W. Fischer and J.D.G. Correia, *J. Mol. Catal.*, **94**, 213 (1994).
9 J.-M. Aubury and S. Bouttemy, *J. Am. Chem. Soc.*, **119**, 5286 (1997).
10 A.E. Shilov and G.B. Shul'pin, *Chem. Rev.*, **97**, 2879 (1997).
11 D.H. Dickman, *Chem. Rev.*, **94**, 569 (1994).
12 D.H.R. Barton, S.D. Beviere, W. Chavasiri, E. Csuhai and D. Doller, *Tetrahedron*, **48**, 2895 (1992).
13 M. Faraj and C.L. Hill, *Chem. Commun.*, 1487 (1987).
14 S.-I. Murahashi, Y. Oda, T. Naota and N. Komiya, *Chem. Commun.*, 139 (1993).
15 J.-I. Tateiwa, H. Horiuchi and S. Uemura, *Chem. Commun.*, 2567 (1994).
16 T. Punniyamurthy, S.J.S. Kalra and J. Iqbal, *Tetrahedron Lett.*, **36**, 8497 (1995).
17 V. Dura-Vila, D.M.P. Mingos, R. Vilar, A.J.P. White and D.J. Williams, *Chem. Commun.*, 1525 (2000).
18 J.A.A.W. Elemans, E.J.A. Bijsterveld, A.E. Rowan and R.J.M. Nolte, *Chem. Commun.*, 2443 (2000).
19 N.I. Kuznetsova, N.V. Kirillova, L.I. Kuznetsova and V.A. Likholobov, *J. Mol. Catal. A: Chem.*, **204-205**, 591 (2003).
20 B. Kayan, R. Özen, A.M. Gizir and N.S. Kus, *Org. Prep. Proced. Intern.*, **37**, 83 (2005).
21 H.A. Burton and I.V. Kozhevnikov, *J. Mol. Catal. A: Chem.*, **185**, 285 (2002).
22 R.L. Holliday, B.Y.M. Jong and W.J. Kolis, *J. Supercritical Fluids*, **12**, 255 (1998).
23 D. Tromans, *Ind. Eng. Chem. Res.*, **39**, 805 (2000).
24. G.G. Hawley, Condensed Chemical Dictionary, Van Nostrand Reinhold Company Inc., New York, USA, edn. 10 (1981).
25 L.D. Ride, CRC Handbook of Chemistry and Physics, CRC Press, Inc., Physical Constants of Organic Compounds, edn. 72 (1991-1992).
26. R.M. Silverstein, G.C. Bassler and T.C. Morril, Spectrometric Identification of Organic Compounds, Van Nostrand Reinhold Company Inc., New York, USA, edn. 5 (1981).
27. C.J. Pouchert, The Aldrich Library of NMR Spectra, Aldrich Cemical Company Inc., USA, edn. 2 (1983).
28. R.J. Keller, The Sigma Library of FT-IR Spectra, Sigma Chemical Company Inc., USA, edn. 1 (1986).

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