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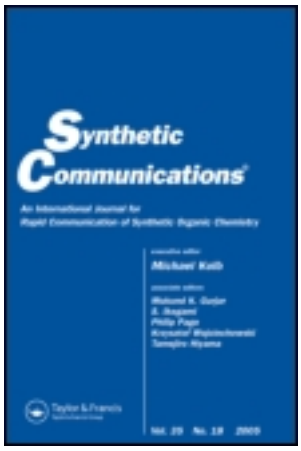

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Microwave Promoted Rapid Oxidation of Alcohols Using Cobalt Nitrate Hexahydrate Supported on Silica Gel Under Solvent Free Conditions

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Published online: 16 Aug 2006.

To cite this article: A. R. Kiasat , F. Kazemi & M. Rafati (2003): Microwave Promoted Rapid Oxidation of Alcohols Using Cobalt Nitrate Hexahydrate Supported on Silica Gel Under Solvent Free Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:4, 601-605

To link to this article: http://dx.doi.org/10.1081/SCC-120015814

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SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 4, pp. 601–605, 2003

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ABSTRACT

A new method for oxidation of alcohols into the corresponding carbonyl compounds by treatment with cobalt nitrate hexahydrate adsorbed on silica gel is described. This reagent can be used as an effective and mild oxidizing agent for this transformation under microwave irradiation in dry media, and high yields. Over oxidation of the formed aldehydes was not observed.

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DOI: 10.1081/SCC-120015814 0039-7911 (Print); 1532-2432 (Online)
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Heterogeneous organic reactions that are facilitated by supported reagents on porous solids and assisted by microwaves, in particular, have developed successfully and in the past few years there has been a tremendous interest in this area.[1,2] Since only the polar reactants adsorbed on mineral surfaces absorb microwave energy, a variety of reagent doped on such supports can be utilized for the enhancement of organic reactions using a household microwave oven. These solvent-free MW-assisted reactions[3] provide an opportunity to work with open vessels thus avoiding the risk of high pressure development and increasing the potential of such reactions to upscale.

The oxidation of alcoholic group to carbonyl functionality is an important reaction in organic synthesis and several methods are available to accomplish this conversion under a variety of reaction conditions. Because of its important role in synthetic chemistry, this reaction continues to receive attention from the chemists in search for newer and selective methods of oxidation.[4,5]

Metallic nitrates can be used as mild oxidizing agent, but little attention has been paid to this potential in organic synthesis.[6–9] Laszlo and Cornelis,[6,7] have reported on appreciably unstable Fe(III) nitrate impregnated on K10 bentnite clay, as a supported metal nitrato complex for the oxidation of alcohol to carbonyl compound. They have reported that, satisfactory results have been obtained with a variety of secondary aliphatic, alicyclic, and benzyl alcohol, and with primary benzyl alcohol. With primary aliphatic alcohol, complex mixtures of products was obtained. In 1997, a report by Varma and Dahiya[2] outlined that clayfen can be oxidize alcohols upon exposure to microwaves under solvent free conditions, also the limitation with aliphatic alcohol still persists and the protocol gives a mixture of compounds. Nishiguchi and Asano[8,9] have supported some metal nitrates on silica gel and used those as oxidizing agents for the oxidation of benzylic alcohols under nitrogen atmosphere. They have reported that activity of the oxidizing agents depended on reaction temperature. By these facts in mind and also reports[7] about high reactivity of bidentate form of nitrate anion in some metal nitrates such as cobalt nitrate, we now wish to report herein a facile and selective oxidation of alcohols to carbonyl compounds using cobalt nitrate hexahydrate supported on silica gel ($Co(NO_3)_2$/Silica gel) under solvent-free conditions in a process that is accelerated by microwave irradiation.

The oxidizing reagent was easily prepared by addition of silica gel to a solution of cobalt nitrate in acetone. Solvent was evaporated and the powdered reagent was dried under reduced pressure. This oxidizing agent was stable and could be stored in air at room temperature without losing

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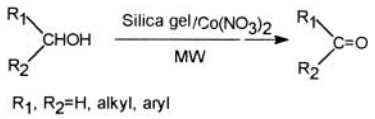

Table 1. Oxidation of alcohols to carbonyl compounds under microwave irradiation.[a]

Entry	Substrate	Time (min)	Yield (%)[b]
1	$PhCH_2OH$	9	91
2	3-Me $OPhCH_2OH$	12	90
3	4-Me $OPhCH_2OH$	8	93
4	4-Me $PhCH_2OH$	8	90
5	4-$BrPhCH_2OH$	14	87
6	2-$ClPhCH_2OH$	12	89
7	$CH_3(CH_2)_6CH_2OH$	14	88
8	Ph–CH=CH–CH_2OH	10	92
9	$PhCH(OH)CH_3$	9	91
10	PhCH(OH)Ph	11	91
11	4-$ClPhCH(OH)CH_3$	14	89
12	$PhCH_2CH(OH)CH_2Ph$	17	85
13	$CH_3(CH_2)_5CH(OH)CH_3$	12	90
14	Cyclohexanol	12	89
15	Cycloheptanol	13	87
16	PhCH(OH)COPh	18	86

[a]Were confirmed by comparison with authentic sample (IR and NMR).
[b]Yield of isolated pure carbonyl compound.

its activity. The procedure involves a simple mixing of neat alcohols with ($Co(NO_3)_2$/Silica gel) and irradiated the mixtures in a microwave oven for the time being specified in Table 1. Several experiments were performed, at various powers and irradiation times, in order to find the most adequate condition for this reaction under microwave irradiation. Oxidizing reagent to substrate ratio of 2:1 and the maximum power out put of 200 W was found to be the optimal condition.

Our experiments show that not only primary and secondary benzylic alcohols but also aliphatic alcohols underwent oxidation to the corresponding carbonyl compounds in high yields with a short time of irradiation. It is noteworthy that further oxidation of obtained aldehydes to their carboxylic acids or cleavage of double bonds of α-β- unsaturated

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Table 2. Oxidation of alcohols to carbonyl compounds under conventional heating.[a]

Entry	Substrate	Time (h)	Yield (%)
1	$PhCH_2OH$	5	96
2	$CH_3(CH_2)_6CH_2OH$	5	65
3	4-ClPhCH(OH)CH_3	5	80
4	$CH_3(CH_2)_5CH(OH)CH_3$	5	75

[a]The alcohol was thoroughly mixed with the oxidizing agent and heated at 80°C under solvent free conditions.

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alcohols were not observed. It was found that the yield of reaction in the absence of silica gel was very low.

To show the dramatic acceleration in the rate of oxidation due to microwave irradiation, under the same experimental condition, several alcohols were heated just by conventional heating. However, only good yields of products were obtained in comparably very long time (Table 2).

As previous reports,[7] it is probable that cobalt nitrate hexahydrate supported on silica gel is serve as a source of nitrosonium ions and the oxidation reaction presumably proceeds via the intermediacy of nitrous esters.

In conclusion, the present procedure of solid phase oxidation of alcohols provides a general methodology. The application of microwave offers a very quick and clean method for this conversion. The operational simplicity, selectivity, use of inexpensive reagent, high yields in significantly short reaction time, can make this procedure a useful and attractive alternative to the currently available methods.

EXPERIMENTAL

General

All yields refer to isolated products. Products were characterized by comparison of their physical data, IR and ^{1}H NMR spectra with known samples. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

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General Procedure for the Oxidation of Alcohols

Silica gel was added to a solution of cobalt nitrate hexahydrate in acetone (1.0 mmol g^{-1} SiO_2). The mixture was evaporated and the residue was finally dried in the presence of P_2O_5 under vacuum at 45°C overnight. Alcohol (1 mmol) was thoroughly mixed with the oxidizing agent (2.582 g, 2 mmol). The resulting mixture was then taken in a Pyrex Erlenmeyer flask (25 mL) and irradiated in a commercial microwave oven (200 W) for the specified period of time (Table 1). The reaction mixture was then allowed to reach room temperature. The inorganic support was separated by filtration after eluting the product with CCl_4. The obtained product after evaporation of the solvent was dried over anhydrous sodium sulfate to afford the TLC and ^{1}H NMR pure carbonyl compound in 85–93% isolated yield.

ACKNOWLEDGMENT

We would like to acknowledge the partial support of this work by Ghachsaran Islamic Azad University Research Council.

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Received in the UK December 3, 2001

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