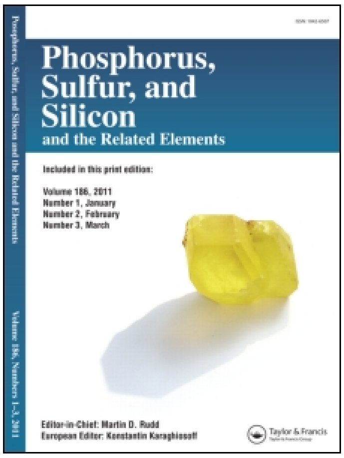

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SELECTIVE OXIDATION OF BENZYLIC ALCOHOLS USING CAN SUPPORTED ONTO SILICA GEL UNDER MICROWAVE IRRADIATION

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Cerium ammonium nitrate (CAN) adsorbed on HNO_3/silica gel is a mild reagent for selective oxidation of benzylic alcohols to the corresponding aldehydes under microwave irradiation in solventless system.

Keywords: Benzylic alcohols; CAN; microwave irradiation; oxidation

The oxidation of alcohols to cabonyl compounds is an important transformation of organic synthesis, and several methods have been explored to accomplish such a conversion.[1] However, there is a constant demand to develop more selective synthetic methods that are able to discriminate efficiently between various functional groups and be relatively ecofriendly. Therefore, selective methods allowing for oxidation of primary benzylic alcohols to aldehydes without overoxidation to carboxylic acids and without competitive oxidation of secondary or nonbenzylic alcohols remain challenging. So far relatively few procedures are available for this type of selectivity.[2]

During the past few years, cerium ammonium nitrate (CAN) has become a synthetic reagent and catalyst of growing importance.[3] Recent years have witnessed a phenomenal growth in the use of high surface area inorganic solids as reaction media for organic transformation.[4] The advantages of the reactions are that they provide enhanced reaction rates, greater selectivity, and manipulative simplicity. The use of microwave irradiation to deliver energy for organic reactions has increased in popularity in recent times.[5] We[6] and others[7] have found that

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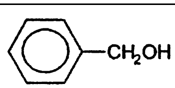
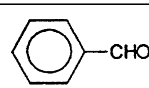
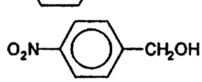
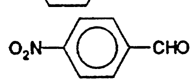
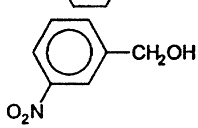
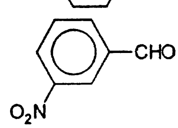
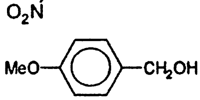
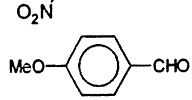
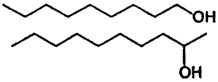
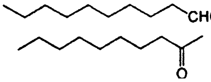
the coupling of microwave irradiation with the use of solid supports facilitates numerous chemical transformations.

In this article we describe a new method for the selective oxidation of benzylic alcohols to the corresponding aldehydes using CAN supported onto HNO_3/silica gel as a support and cocatalyst under microwave irradiation. As a starting point we used CAN as an oxidant for oxidation of benzylic alcohol under microwave irradiation in solventless system. In this case, thin layer chromatography (TLC) analysis indicated the presence of unreacted alcohol. Solvent-free conditions, using 2 equiv. of CAN supported onto silica gel under microwave irradiation gave a mixture of benzaldehyde and unreacted benzyl alcohol. However, when we used a drop of HNO_3 on silica gel under the above condition benzyl alcohol was quatitatively oxidized to benzaldehyde without any noticeable overoxidation to benzoic acid, even with an excess of CAN. Moreover, primary aliphatic and allylic alcohols, and even secondary benzylic alcohols, are oxidized with much lower efficiency under the same reaction conditions (Table I, entries 5 and 6). This observation suggested a possible chemoselective oxidation of primary benzylic alcohols in the presence of alyphatic and secondary ones. Indeed the present oxidation system is prone to be exceptionally chemoselective. The reaction of 1:1 mixture of benzyl alcohol and 1-phenyl ethanol with our reagent resulted in the complete conversion of the benzyl alcohol to benzaldehyde, whereas virtually no ketone could be detected by TLC. To establish the generality of

TABLE I Oxidation of Benzylic Alcohols to Aldehydes

Entry	Substrate	Reaction time (min)	Product	Yield[a] (%)
1		5		89
2		4		91
3		5		90
4		8		75
5		5		Trace
6		5		Trace

[a]Yields refer to isolated products.

the method for benzylic alcohols, various benzylic alcohols were successfully converted to their corresponding aldehydes using CAN supported onto HNO_3/silica gel in short reaction time and excellent yields.

In summary, this methodology allows a convenient, high-yielding, relatively benign selective and chemoselective procedure for oxidation of benzylic alcohols. The ease of workup and availability of reagents are the other advantages of this method. These features should make it of significant synthetic value.

EXPERIMENTAL

CAN, alcohols, and silica gel were purchased and used as received. All products were known and identified by comparison of their physical data with those of authentic samples.

General Procedure for the Oxidations

In a beaker a drop of conc. HNO_3 was added to silica gel (1 g) and mixed thoroughly using a spatula. To this HNO_3/silica gel, CAN (2 mmol) and neat benzylic alcohol were added and mixed thoroughly. The beaker was placed in a household microwave oven for the indicated time (Table I). The progress of reaction was monitored by TLC using hexane:EtOAc (8:2) as eluent. After the completion of the reaction, to the residue CH_2Cl_2 (10 ml) was added and the reaction mixture was filtered off. The filtrate was evaporated to dryness under reduced pressure, and the crude was directly subjected to column chromatography using hexane:EtOAc (8:2) as eluent to yield the corresponding aldehydes (Table I).

$$ArCH_2OH \xrightarrow[HNO_3/\text{ silica gel}]{CAN} ArCHO$$

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