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## Note

# Microwave thermolysis-Part IX: A selective and rapid oxidation of benzylic alcohols using clay supported ammonium nitrate

H M Meshram*, B Muralidhar, B Eeshwaraiah, K Ramesh Babu, D Aravind & J S Yadav

Organic Division-I, Discovery Laboratory, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Email: hmmeshram@yahoo.com

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The oxidation of a variety of benzylic alcohols to carbonyl compounds using clay-supported ammonium nitrate "clayan" under microwave irradiation is described. The selectivity and non-solvent condition are the important features of the procedure.

**Keywords**: Microwave thermolysis, benzylic alcohols, oxidation, clay-supported ammonium nitrate

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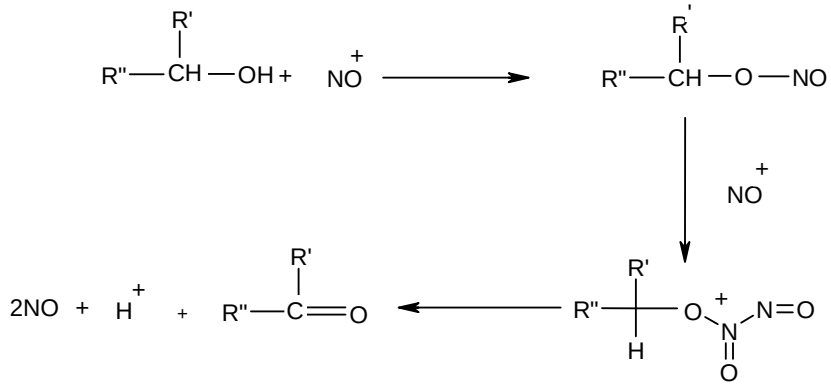
The oxidation[1] of alcohol to carbonyl functionality is a useful transformation in organic synthesis due to which the oxidative reagents have got more importance. Classical reagents utilize the salt of heavy metals, such as $MnO_2$, $KMnO_4$, $CrO_3$, $K_2CrO_4$, $K_2Cr_2O_7$. Though these are used in laboratory or in industry, their preparation and experimental conditions have negative influence on the practical results. Further improvements in the methods were made using supported catalysts[2], because of their convenience and selectivity. Particularly, the supported metal oxides[3], and nitrates[4a,b,c] have proved their oxidizing power in different mode[4d] of reaction. But all these methods encounter the problem of the waste effluent or the presence of heavy metal, which are detrimental to the environment. Moreover, some of the methods suffer from over oxidation and lack of selectivity in the presence of other protected functional groups. In view of this approach was to devise selective oxidation procedure with simple and non-metallic reagent.

Recently, the clay supported reagents[5a,b] in combination with microwave[6] is an area of growing interest because of reduction in time, non-solvent condition and simple work-up. In the course of our study in the area of solid supported[7] and microwave assisted[8] reactions, we have demonstrated "clayan" for dethioacetalization[7d], MPM deprotection[8b] and deoximation[9a,b]. Herein we wish to report a rapid and selective oxidation of alcohols using "clayan" under microwave irradiation and solvent free condition.

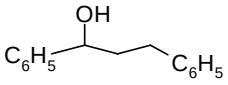
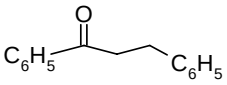
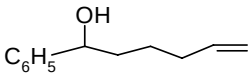
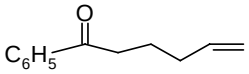
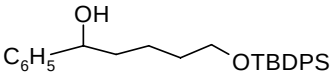
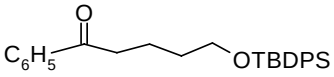
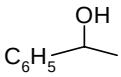
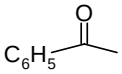
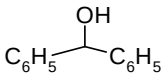
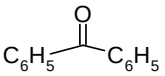
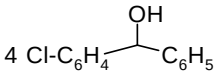
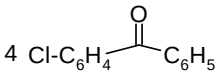
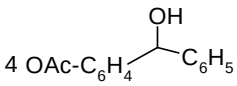
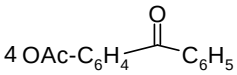
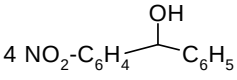
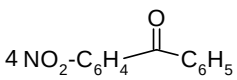
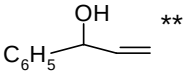
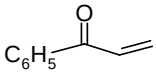
Initially, the reaction of benzyl alcohol was carried out with "clayan" (1:7 ratio of ammonium nitrate present in reagent) in reflux benzene. But the reaction remains incomplete, even after stretching the reaction time (15 hr, 40%). The microwave technique was utilized and the reaction was completed in 90 sec with less ratio of reagent (1:4). In the similar way, the oxidation of other alcohols were carried out successfully. It was noticed that the benzylic alcohols oxidize selectively and the products were also leached by simple extraction (**Table I**). It was remarkable to




R'= H,alkyl
R"= aryl

**Scheme I**

**Table I** — Oxidation of alcohols to carbonyls using “”Clayan”” under microwave irradiation

| Alcohols | Products | Time (sec) | Yields (%)* |
|---|---|---|---|
| $C_6H_5$-$CH_2OH$ | $C_6H_5$-CHO | 90 | 86 |
| 4- $NO_2$-$C_6H_4$-CH2OH | 4- $NO_2$-$C_6H_4$-CHO | 90 | 81 |
| 4- OMe-$C_6H_4$-CH2OH | 4- OMe-$C_6H_4$-CHO | 100 | 83 |
|  |  | 120 | 80 |
|  |  | 120 | 73 |
|  |  | 90 | 70 |
|  |  | 120 | 85 |
|  |  | 110 | 83 |
|  |  | 115 | 80 |
|  |  | 110 | 81 |
|  |  | 115 | 80 |
|  ** |  | 120 | 70 |

* All the products exhibited physical and spectral (NMR, IR & Mass) properties in accord with the assigned structures.

** Ratio of alcohols: reagent is 1:7

note that unlike other method the double bond, O-TBDPS and O-acetyl protection remain unaffected under the same reaction conditions. It is well known that the nitrates in the presence of clay, produce nitrosonium ion[4c] (NO*). This is tested with “clayan” by the reaction of thiophenol into disulphide[4c]. So the

reaction may proceed via nitrosonium intermediate (**Scheme I**).

In conclusion, a rapid, highly selective and environmentally safe procedure has been demonstrated for the oxidation of benzylic alcohols. Easy preparation of reagent, self-destroying nature and solvent free condition make the method more attractive.

## Experimental Section

Boiling points and melting points are uncorrected. Melting points were recorded on Buchi R535 apparatus. All the starting materials were commercially available and used without further purification. OTHP ethers, acetals and acetonides were prepared following the literature procedure. The reagent "clayan" was prepared by the impregnation of ammonium nitrate on montmorillonite-K10, which was purchased from Aldrich Chemical Limited. IR spectra were recorded on a IR Nicole 740 FT IR spectrometer, $^1$H NMR spectra were recorded on FT (200 Gemini) spectrometer. Mass spectra were recorded on either Micro mass 7070 h or Finnigan Mat 1020 B mass spectrometer operating at 70 eV. TLC was performed on pre-coated silica gel 60f 254 (0.5 mm) glass plates.

**General procedure for the oxidation**. In a typical procedure, alcohol (1 mmole) was mixed with clay-supported ammonium nitrate "clayan" (640 mg, 4 mmoles of ammonium nitrate in reagent) in solid state, was transferred to a test tube and subjected to microwave irradiation (BPL make, BMO 700T, 650W, operating at frequency of 2450 MHz). Reaction was monitored by TLC (hexane-ethyl acetate; 80:20). After completion of reaction, the mixture was extracted with DCM (3×20 mL). Evaporation of the solvent gives carbonyl compounds in good yield. Further products were purified by passing through a short column of neutral alumina using hexane : ethylacetate, (90:10) as eluent.

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