



Dinitrogen tetroxide supported on solid (shell powder) for oxidation of alcohols

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ABSTRACT

The study dinitrogen tetroxide gas (N_2O_4) on solid ground here shell powder consolidation, this method has many advantages that can be easier to oxidation and nitration of organic compounds and transport easier N_2O_4 noted. After supported process and evaporation of the solvent at room temperature, supported Dinitrogen tetroxide on shell powder (PS- N_2O_4), used for the oxidation of aromatic alcohols.

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KEYWORDS

Dinitrogen tetroxide (N_2O_4);
Shell powder;
Lead (II) nitrate;
Alcohol.

INTRODUCTION

Dinitrogen tetroxide and its complexes have found wide applications in organic transformations^[1]. Dinitrogen tetroxide (N_2O_4) is the chemical compound that forms an equilibrium mixture with nitrogen dioxide (N_2O_4/NO_2)^[2]. Dinitrogen tetroxide as an important industrial chemical is commercially supplied at low price in a cylinder, and can be used directly or in the form of liquid. Since liquid N_2O_4 evaporates at 21.15 C under atmospheric pressure, $M(NO_3)_x.yN_2O_4$ is a very convenient and thermally stable source of N_2O_4 ^[1].

In order to overcome the problems of corrosive and toxic dinitrogen tetroxide and high reactivity of gaseous N_2O_4 , and also to be able to product pure solution of alcohol oxidation under heterogeneous we decided to prepare shell powder supported N_2O_4 as a heterogeneous reagent. Its high reactivity which usually causes undesired side reactions^[3].

In recent years some reports were published on the use of N_2O_4 complexes of organic and inorganic

compounds such as 18-crown-6/ N_2O_4 ^[4], polyvinylpyrrolidone/ N_2O_4 ^[5], $M(NO_3)_x.y N_2O_4$ ^[6], activated charcoal/ N_2O_4 ^[7], N_2O_4 /SiO_2 ^[8], silica acetate- N_2O_4 ^[9], calix4-aren/ N_2O_4 ^[10], DMF- NO_2 ^[11], and (tributyl phosphate- NO_2 , polyethylene glycol- NO_2 , dioxane- NO_2)^[12] as useful reagents that solve many difficulties in handling and increase selectivity of organic reactions.

The study dinitrogen tetroxide gas (N_2O_4) on solid ground here shell powder. After supported process and evaporation of the solvent at room temperature, supported Dinitrogen tetroxide on shell powder (PS- N_2O_4), used for the oxidation of aromatic alcohols.

EXPERIMENT

Preparation of N_2O_4

The lead (II) nitrate dried in an oven at 120 °C for three days, and 45.0 g of it add to a 250-mL flask. The flask connected to refrigerant pipes and Erlenmeyer. The lead (II) nitrate was heated with a Bunsen burner.

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Brownish red NO_2 - N_2O_4 gas evolved and it collect in the Erlenmeyer^[6]. Erlenmeyer is at temperature 0°C .

Preparation of shell powder -Supported N_2O_4

Add to 2ml of liquid N_2O_4 , 2g shell powder (shell powder drying at 120°C) and 5ml dichloromethane. After 1 h, solvent was evaporated at room temperature. Produced is shell powder supported N_2O_4 as white cream powder (2.615 g).

Exemplary FTIR spectrum of shell powder supported N_2O_4 is shown in Figure 1.

Oxidation of alcohol under solvent free

A mixture of alcohols (1 mmol) and Shell powder-supported N_2O_4 (PS- N_2O_4) (0.66 gr) was ground at room temperature. The progress of the reaction was monitored by TLC. After the completion of the reaction ether (30 mL) was added and filtered through a silica gel. The combined filtrates were evaporated. The filter cake was purified by a short pad washed with n-Hexane–Ethyl acetate (4: 1) (50 mL) and the solvent was evaporated to afford carbonyl compound in high yield.

RESULTS AND DISCUSSION

Gaseous dinitrogen tetroxide was also known to

be a good reagent of alcohol to corresponding aldehyde and ketone^[1]. Shell powder-supported N_2O_4 (PS- N_2O_4) is a safe, cheap and easily prepared source of N_2O_4 . The IR spectrum of Shell powder-supported N_2O_4 showed a strong absorption at 1605 cm^{-1} that related to is asymmetric stretching vibration of the N-O^[7]. In this work we used shell powder/ N_2O_4 to oxidation of alcohol at room temperature. By use of this reagent, oxidation different alcohols which results are shown in TABLE 1.

The rate of oxidation and yield of product depended on the nature of the substrate and reaction condition. Oxidation of benzylic alcohols proceeded more rapidly than the oxidation of aliphatic alcohols (TABLE 1). In the oxidation of benzyl alcohols to benzaldehyde, when there is an electron releasing group, the rate and yield of the reaction increased. 4-Nitro benzyl alcohol is oxidized to its corresponding aldehyde within a longer time and 85% yield. Primary and secondary aliphatic alcohols are oxidized to the corresponding carbonyl compounds under these conditions. The reactions are relatively clean with no tar formation and no over oxidation to carboxylic acids. The reaction of cinnamyl alcohol gave cinnamaldehyde with a high yield without cleavage of benzylic double bond.

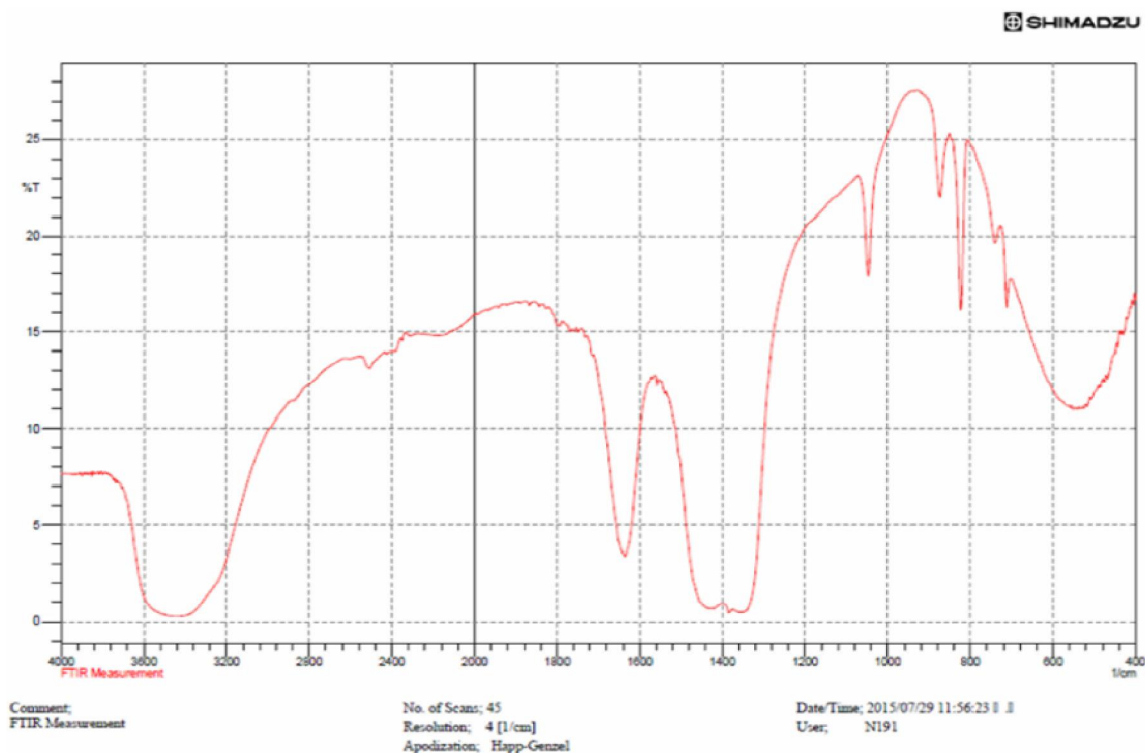
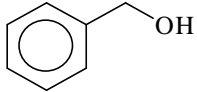
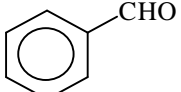
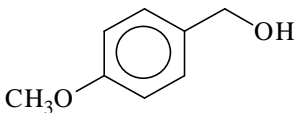
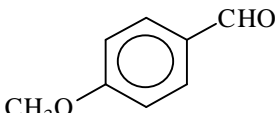
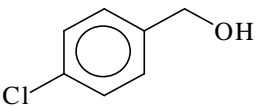
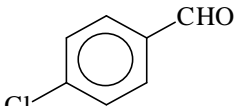
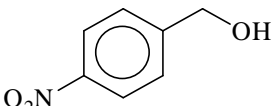
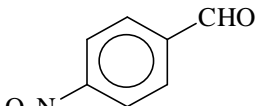
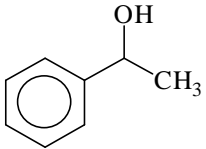
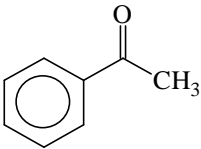
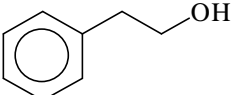
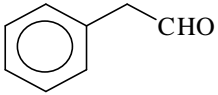
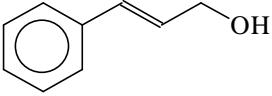
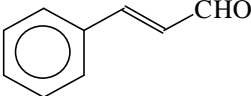
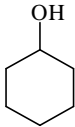
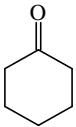
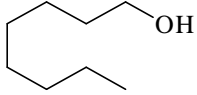
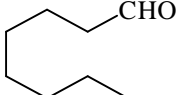
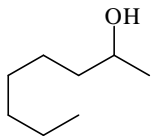
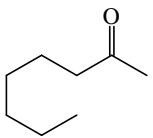


Figure 1 : FTIR spectrum of shell powder supported N_2O_4

Entry	Substrate	Product	Time(min)	Yield%
1			5	95
2			2	90
3			10	85
4			60	95
5			5	85
6			30	85
7			15	85
8			45	60
9			50	60
10			50	55

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In this study we have introduced a new reagent for alcohol oxidation of under nonaqueous and heterogeneous condition. Due to the lower reactivity of this reagent compared to dinitrogen tetroxide, alcohol can be selectivity converted into their corresponding aldehyde or ketone of the reagent and reaction condition.

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