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Copper(II) nitrate on Clay (Claycop)–Hydrogen Peroxide: Selective and Solvent-free Oxidations Using Microwaves†

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Abstract: Claycop [copper(II) nitrate on clay]-hydrogen peroxide is an efficient and selective oxidizing reagent for a variety of compounds under solvent-free conditions using microwaves.

The oxidation reactions are important transformations in organic synthesis[1a] and continue to attract the attention of chemists.[1b] Metal ions play a significant role in many of these reactions[2a] as well as in biological dioxygen metabolism.[2b] Copper(II) acetate and hydrogen peroxide have been used to produce a stable oxidizing agent, hydroperoxy copper(II) compound,[3] which is also obtainable from copper(II) nitrate and hydrogen peroxide (Eqn.).[4] The ensuing nitric acid requires neutralization by potassium bicarbonate to maintain a pH ~5.

$$2Cu(NO_3)_2 + H_2O_2 + 2H_2O \longrightarrow 2CuO_2H + 4HNO_3 \qquad \textbf{(Eqn.)}$$

In recent years, the organic reactions on mineral supports[5] have gained popularity because of their selectivity and associated ease of manipulation. Since only the polar reactants adsorbed on the surfaces of various mineral supports absorb microwaves (MW), a variety of reagents supported on such surfaces can be utilized for the enhancement of organic reactions using a simple microwave oven.[6-8] MW-enhanced chemical reactions,[6-8] especially under solvent-free conditions,[7,8] have several advantages over the conventional reactions in view of the rapid reaction rates attained and higher yields of the pure products formed.

In continuation of our ongoing program on MW-assisted solvent-free reactions, we now report a facile oxidative protocol that utilizes H_2O_2 and copper(II) nitrate trihydrate impregnated on montmorillonite K10 clay (claycop)[9] under microwave irradiation conditions. This rapid method requires no pH control and provides better yields as compared to those obtained by earlier workers using copper-based reagents.[3,4] Triphenylphosphine and hydroquinone are oxidized to triphenylphosphine oxide and *p*-benzoquinone, respectively. The oxidations can be conducted cleanly and in a controlled manner as exemplified by selective oxidation of phenylacetonitrile (entry 3) to phenylacetic acid in 30 sec with 0.46 g of claycop (0.8 mmol of copper(II) nitrate) and to benzaldehyde with 0.92 g of the reagent. The overoxidation of the ensuing aldehydes to the corresponding carboxylic acid is not observed. The reactions conducted by simply admixing various components, copper nitrate/clay/H_2O_2 with the substrates, are relatively sluggish and afford mixture of products in some cases. That the effect may not be purely thermal is evident from the fact that reaction (diphenylacetic acid, entry 2) using the same amount of oxidant and performed at the same temperature of 110 °C (in an oil bath) is not completed even after 10 h.

The experimental procedure involves a simple mixing of neat substrates with claycop (0.46 g per mmol of the substrate) followed by the addition of 30% H_2O_2 (0.1 mL) in an open container. The mixture is placed in an alumina bath inside a microwave oven and is irradiating for 15-90 sec in the solid state.[10] Upon completion of the reaction, monitored on TLC (hexane:AcOEt, 10:1), the product is extracted into methylene chloride and solvent removed to afford pure products. Our results for oxidation of various substrates are summarized in the **Table**.

In conclusion, the solvent-free reactions with claycop/hydrogen peroxide upon MW irradiation are efficient and cleaner oxidative processes when compared to the conventional solution phase or heterogeneous reactions.

Dedicated to Dr. Billy C. Covington, a strong proponent of science, on the occasion of his 50th birthday

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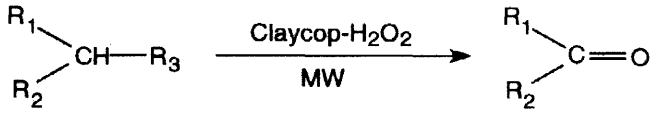

Table: Oxidation of organic substrates by claycop and hydrogen peroxide

Entry	R_1	R_2	R_3	Mole[a] Ratio	Time (sec)	Yields (%)
1	C_6H_5	H	COOH	1:0.8:1	60	83
2	C_6H_5	C_6H_5	COOH	1:0.8:1	90	82
3	C_6H_5	H	CN	1:1.6:2[b]	45	80
4	C_6H_5	H	NH_2	1:0.8:1	30	76
5	C_6H_5	H	Br	1:0.8:1	30	75
6	p-NO_2-C_6H_4	H	H	1:1.6:2	90	69
7	Triphenylphosphine			1:0.8:1	15	85
8	Hydroquinone			1:0.8:1	30	71

[a]Substrate:copper(II) nitrate:hydrogen peroxide [0.46 gram of claycop contains 0.8 mmol of copper(II) nitrate].
[b]Using 0.8 mmol equivalents of the copper(II) nitrate results in the formation of phenylacetic acid.

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