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Green twist to an old theme. An eco-friendly approach*

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Abstract: Owing to present environmental awareness, attempts are being made toward the evolution of environmentally benign processes using solid-supported reagents and microwave-assisted reactions. A newly developed, nonmetallic oxidative reagent, “clayan”, has been exploited for various reactions such as deprotection, oxidation, oxidative coupling, and nitration and bromination of activated and deactivated arenes. In another green chemistry endeavor, reactions such as reduction and cyclization have been successfully carried out in dry media under microwave irradiation. The nonsolvent reaction, experimental simplicity, and enhanced selectivity are the main attractive features of the approach.

INTRODUCTION

With the increase in global population, obviously demands have increased to meet requirements. Industries are producing in bulk at the cost of huge waste, which makes the environment polluted. The term “green chemistry” [1] has come into existence to control this detrimental phenomenon. Owing to environmental awareness [2], chemists are forced to change old themes with new twists to develop environmentally friendly processes. Keeping the theme of green chemistry in mind, this global change can be brought out by the following facts:

- increasing the effective surface area for reaction
- changing the mode of reaction

INCREASING THE EFFECTIVE SURFACE AREA FOR REACTION

Most of the organic reactions that are carried out using unsupported reagents frequently either fail or result in the formation of mixer of products. However, using solid-supported reagents [3], many reactions can be carried out cleanly and rapidly, realizing high yield under mild conditions. This is because of the increase in the effective surface area available for the reaction. So the amount of catalyst can be reduced when it is dispersed on the support. In the case of solid acids, it can be reused again, avoiding the use of corrosive acids and waste treatment. Because of distinct advantages, these processes can make a great contribution to green chemistry. Propelled by environmental protection awareness, we have developed a new nonmetallic reagent “clayan” [4] clay-supported ammonium nitrate, and its chemical properties have been exploited for various reactions.

A variety of thioacetals and dithianes are deprotected into their parent carbonyl compounds under mild conditions using clayan in dichloromethane [4].

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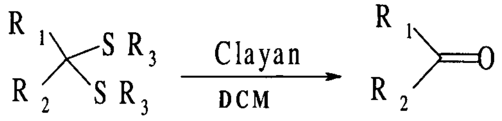
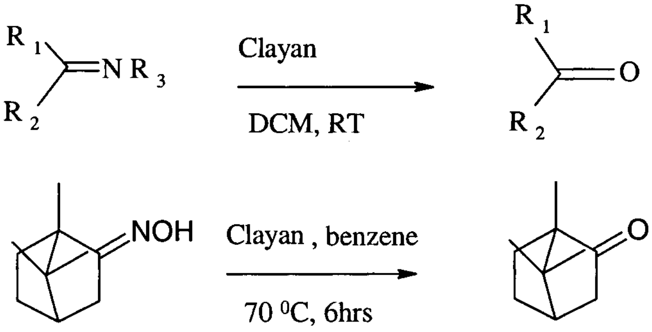


R_1 = H, Alkyl. R_2 = H, alkyl, aryl. R_3 = $-(\text{-CH}_2)_3-$, Et, Et.

Electron-rich oximes are selectively deprotected using clayan in dichloromethane under mild conditions [5]. It is observed that for the other protecting groups, such as silyl ethers, esters, acetonides, BOC, acetate, and benzyl ether, double and triple bonds remain unaffected.

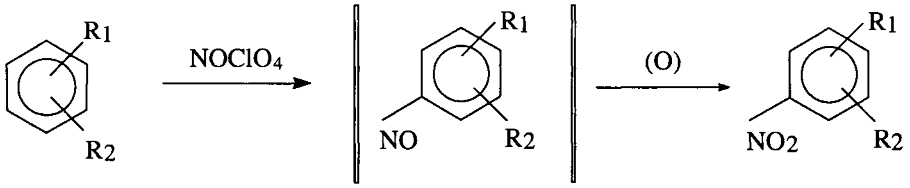


A variety of isothiocyanates have been prepared by the decomposition of dithiocarbomates with claycop [6] in toluene at room temperature (RT) [7]. The procedure is also suitable for the preparation of the amino acid isothiocyanate.

$$\text{R-CH}_2\text{-NHCS}_2^-\ \text{NH}_4^+ \xrightarrow[\text{Benzene/ toluene}]{\text{CLAY COP}} \text{R-CH}_2\text{-N=C=S}$$

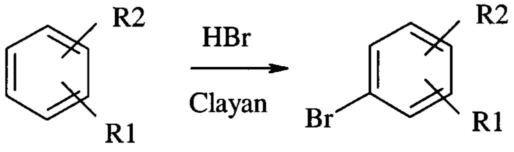
Nitration of activated and deactivated arenes is performed using clayan in the presence of perchloric acid [8]. Compounds bearing functional groups such as aldehyde, amide, and nitrile can be directly nitrated without affecting the functionality. This method also manipulates to drive the reaction toward mono nitration.

$$\text{NO+} \quad + \quad \text{HClO}_4 \longrightarrow \text{NOClO}_4$$



R_1, R_2 = alkyl, aryl, ring-activating or deactivating substitutions.

Furthermore, the oxidative property of clayan has been utilized for the bromination of arenes in combination with HBr in aqueous media [9]. The formation of mono or dibrominated product can be manipulated by controlling the reaction conditions



R_1 = H, activating group. R_2= H, activating group, deactivating group.

CHANGING THE MODE OF REACTION

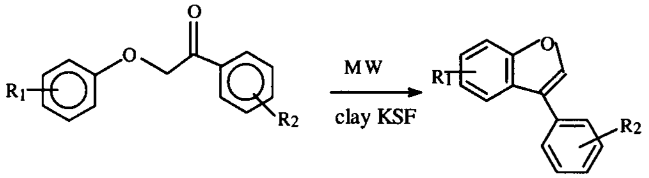
Recently, microwave [10] has been proven as a very important tool for functional group transformation when compared to the conventional method. These reactions are very fast, without solvent, and the workup is very simple. We have successfully attempted some reactions under microwave irradiation.

The selective deprotection of MPM ethers has been carried out using clayan under microwave (MW) in solvent conditions with 1:7 ratio [11]. Other protecting groups, such as silyl ethers, esters, acetonides, BOC, acetate, and benzyl ether, remain unchanged. Double and triple bonds also remain unaffected.

$$\text{R-CH}_2\text{-OMPM} \xrightarrow[\text{MW}]{\text{CLAYAN}} \text{R-CH}_2\text{-OH}$$

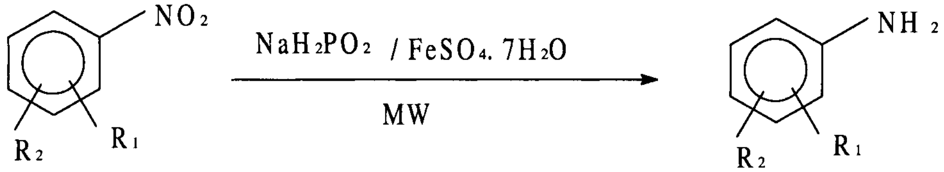
R = alkyl, aryl, acetate, silyl ethers, esters, double bond or triple bond or benzyl ether.

3-Substituted benzofurans have been prepared by the cyclodehydration of α-phenoxy-acetophenone using clay under microwave irradiation [12]. The present method has advantages over the other methods, such as easily accessible catalyst, dry condition, and formation of exclusively 3-substituted benzofurans, which are otherwise difficult to prepare.



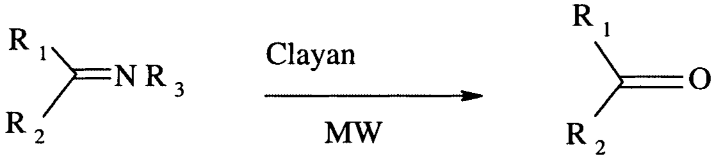
R_1 = H, R_2 = i-pr, Aryl,Cl,Br, R_2 = Me,Ph.

Nitro arenes are reduced to amines, using sodium hypophosphite under microwave irradiation in dry media [13]. Whereas, the oximes (R_1 or R_2) are dehydrated to nitriles in the same reaction conditions.



R, R_1 = H, CH_3, OH, $CONH_2$, C_6H_5, COOH, CN, NH_2.

Carbonyls are deprotected in MW. Carbonyls are regenerate from their derivatives, such as oximes, hydrozones, semicarbazones, using clayan in dry media. In solvent reaction works only for electron-rich oximes [14].

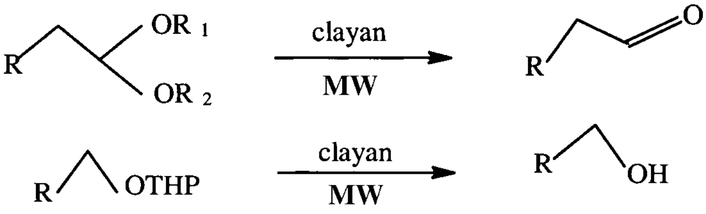


Oxidative coupling of thiol and thiol acetates in dry media leads to disulphide using clayan in dry media [15,16].

RSH + Clayan ⟶ RS SR

RSCOR + Clayan ⟶ RS SR

O-THP ethers, acetals, and acetonides are selectively cleaved using clay-supported ammonium nitrate “clayan” in dry media. Groups such as esters, ethers, and double and triple bonds are sustained by this method [17].



R = alkyl, aryl; $R_1 = R_2$ = Et, $CH_2\text{-}CH_2$

Deoxygenation of various sulfoxides using $NaH_2PO_2\text{-}FeSO_4.7H_2O$/alumina under microwave irradiation leads to sulfide. Dibenzyl sulfoxide can be deoxygenated without any side-products, which is otherwise difficult.

$$\text{R-SO-R}' \xrightarrow[\text{MW}]{\text{NaH2PO2-FeSO4.7H2O/ alumina}} \text{R-S-R}'$$

Thiocyanates and isothiocyanates are prepared by the reaction of potassium thiocyanate with alkyl bromides in dry media under microwave irradiation. It is observed that at RT the reaction gives only thiocyanates and after irradiation isomerizes to isothiocyanate.

$$\text{R-X} \xrightarrow[\text{Clay, RT}]{\text{KSCN}} \text{R-SCN} \xrightarrow[\text{MW}]{} \text{R-NCS}$$

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