COMPARISON OF CLINOPTILOLITE, ANALCIME AND YUGAWARALITE FOR SYNTHESIS OF UNSATURATED 5(4H)-OXAZOLONES IN SOLVENT-FREE CONDITION AND MICROWAVE IRRUDIATION

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Abstract: In view of the importance of azlactones as synthons, biological importance of the compounds and the advantages offered by coupling microwave activation with dry media reactions, we report here a solvent-free procedure for the synthesis of 2-phenyl-5(4H)-oxazolones from aldehydes or ketons and hippuric acid using clinoptilolite, analcime and yugawaralite under microwave irradiation according to green chemistry.

Introduction

Clinoptilolite, analcime and yugawaralite are framework aluminosilicates, whose structure is characterized by cavities and channels, where exchangeable cations and water molecules are hosted. These structural features are responsible for the wide industrial applications of zeolites as catalysts and selective absorbers.

Analcime ($NaAlSi_2O_6.H_2O$) is a popular and interesting mineral. It is sometimes known as analcite, although analcime is preferred. It is one of the few minerals that characteristically form their own unique crystal. Analcime is a zeolite having a complex aluminosilicate framework that is common to all leucite- type feldspathoids. The framework is based on corner sharing $(Al,Si)O_4$ tetrahedra, arranged in fourfold, sixfold and eightfold rings. The sixfold rings are arranged axially, forming parallel channels. Analcime's structure, however, has a typical zeolite openness about it that allows large ions and molecules to reside and actually move around inside the overall framework[1].
Yugawaralite ($CaAl_2Si_6O_{16}.4H_2O$) is a rare natural zeolite. The crystal structure was determined by X-ray single crystal diffraction. It has a peculiar topology composed of 5- and 4-memberd rings of tetrahedral and a fully ordered distribution of aluminum atoms in the framework [2].
Clinoptilolite [$(Na,K,Ca)_3Al_3(Al,Si)_2Si_{13}O_{36}$-$12H_2O$] is one of the more useful natural zeolites. It is used in many applications such as a chemical sieve, a gas absorber, a feed additive, a food additive, an odor control agent and as a water filter for municipal and residential drinking water and aquariums. It can easily absorb ammonia and other toxic gases from air and water and thus can be used in filters, both for health reasons and for odor removal[3-4].

5(4H)-Oxazolones are important intermediates in the synthesis of several molecules including amino acids, peptides, antimicrobial or anti-tumor compounds, heterocyclic precursors as well as biosensors coupling and or photosensitive composition devices for proteins. Some oxazolones show a wide range of pharmaceutical properties [5-6].

A number of methods are available for the synthesis of azlactones including the use of acetic anhydride and sodium acetate, acetic anhydride and lead acetate, polyphosphoric acid, sulphur trioxide/dimethyl formamide complex, perchloric acid and carbodiimides.

Recently, synthesis of oxazolones has been reported by using anhydrous zinc chloride or bismuth (III) acetate, as catalysts [7-9].

Nowadays, the microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. This in-situ mode of energy conversion has many attractions for chemists, because its magnitude depends on the properties of the molecules. This allows some control of the material's properties and may lead to reaction selectivity.

There are a variety of methods for carrying out microwave-assisted organic reactions using domestic or commercial ovens. This is basically known as Microwave-induced Organic Reaction Enhancement (MORE) chemistry. Microwave heating has not been restricted to organic chemistry, as various aspects of inorganic chemistry and polymer chemistry have also been investigated[10-11].

Results and Discussion

Clinoptilolite with the simplified formula $(Na,K)_6 Si_{30} Al_6 O_{72} .n H_2O$ is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin. The structure of clinoptilolite is sheet-like. Although still a true tectosilicate where every oxygen is connected to either a silicon or an aluminum ion (at a ratio of [Al +Si] /O =1/2), there still is a sheet-like structural organization. The sheets are connected to each other by a few bonds that are relatively widely separated from each other. The sheets contain open rings of alternating eight and ten sides. These rings stack together from sheet to sheet to form channels throughout the crystal structure.

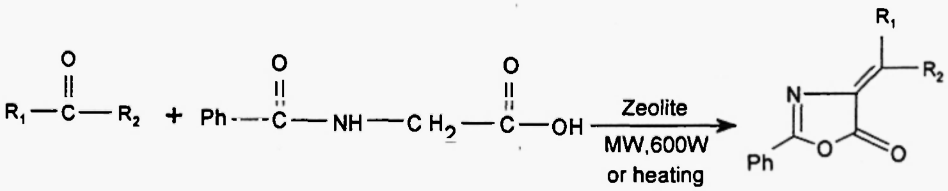
The size of these channels controls the size of the molecules or ions that can pass through them and therefore a zeolite like clinoptilolite can act as a sieve, allowing some ions to pass through while blocking others. A zeolite can be thought of in terms of a house, where the structure of the house (the doors, windows, walls and roof) is the zeolite while the furniture and the people living in, are the water and ammonia molecules and ions that can pass in and out of the structure. Clinoptilolite's sheet-like structure produces the prominent pinacoid faces, the perfect cleavage and the unique luster on those faces.

For most catalytic applications activated zeolites are required. It is ion exchanged to clinoptilolite-NH4$^+$with subsequent release of H_2O and NH_3 upon heat treatment above 700k leading to anhydrous clinoptilolite-H Bronsted centers. Upon dehydroxylation at higher temperature the concentration of Bronsted sites (acidic hydroxyl groups) decreases and Lewis sites are formed [10].

The synthesis of azlactones under M.W irradiation has been reported in open vessels using acetic anhydride, which acts both as reagent and as the organic phase. Acetic anhydride is a well-known toxic reagent and its use for carrying out reactions under microwave irradiation in open vessels would spoil the cavity of the oven and also lead to the emission of acetic anhydride as a supported reagent was explored in continuation of our ongoing work on the use of supported reagents with microwave irradiation.

Hippuric acid is condensed to 2-phenyl-5(4H)-oxazolone using the zeolite (Scheme-1). Then complexation of carbonyl group with cations of zeolite leads to electrophilic assistance during nucleophilic attack on this group and then condensational reaction occurs. Zeolite was used as the catalyst and dehydration reagent (Scheme-2,3).

The activity of clinoptilolite, analcime and yugawaralite for synthesis 5(4H)-oxazolones (**3a-j**) was carried out with two method microwave irradiation and heating. The best results were obtained for clinoptilolite (Table-1,2). It should be mentioned that the yield of isolated products with analcime and yugawaralite in the thermal heating is not much.



(1) (2)

1a) Benzaldehyde	**1f)** 3,4-Dimethoxy Benzaldehyde
1b) 4-Chlorobenzaldehyde	**1g)** 4-(N,N- Dimethylamino)benzaldehyde
1c) 2,4-Dichlorobenzaldehyde	**1h)** Furfural
1d) 3-Nitrobenzaldehyde	**1i)** Thiophencarbaxaldehyde
1e) 4-Methoxybenzaldehyde	**1j)** Cyclohexanone

Scheme-1

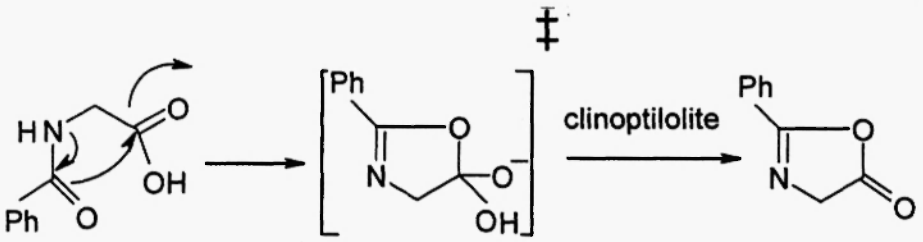
Table-1: Synthesis of 2-phenyl-5(4H)-oxazolone derivatives under solvent-free condition and microwave irradiation using the yugawaralite, analcime, clinoptilolite. (Power = 600W)

Products	R_1	R_2	yug[a]	ana[a]	clino[a]	m.p.(°C)	m.p.(Lit)
2a	H	C_6H_5	50	70	78	160-161	158[12]
2b	H	4-ClC_6H_4	45	65	74	189-190	185[13]
2c	H	2,4-Cl_2 C_6H_3	44	64	72	181-182	183[13]
2d	H	3-$NO_2C_6H_4$	51	71	79	177-178	175-176[14]
2e	H	4-$MeOC_6H_4$	55	75	83	158-159	159[5]
2f	H	3,4-$(OMe)_2C_6H_3$	54	74	82	150-151	150 [6]
2g	H	4-Me_2N C_6H_4	57	77	85	212-213	213-214[14]
2h	H	C_4H_3O	42	62	71	171-172	171[5]
2i	H	C_4H_3S	39	59	68	178-179	180[5]
2j		-$(CH_2)_5$-	50	70	79	138-139	137-138[14]

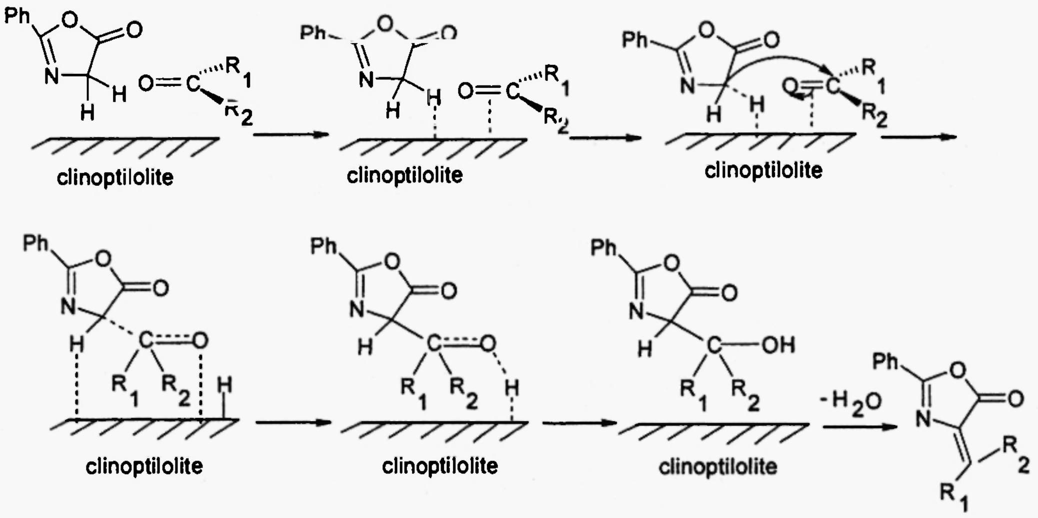
a. yields of isolated products by yugawaralite, analcime, clinoptilolite

Table-2: Comparison of heating condition and microwave irradiation (MW) (power = 600W) using the clinoptilolite **3a-j.**

	Microwave	irradiation		Conventional	heating	
Product	Time(min)	Yield(%)[a]		Time(min)	Temp.(°C)	Yield(%)[a]
2a	20	78		120	120-130	67
2b	22	74		100	120-130	62
2c	25	72		90	120-130	58
2d	25	79		85	120-130	58
2e	10	84		40	120-130	75
2f	12	81		50	120-130	72
2g	7	78		25	120-130	65
2h	9	71		35	120-130	60
2i	9	68		40	120-130	55
2j	25	79		150	120-130	70



Scheme-2



Scheme-3

Experimental Section

Melting points were determinated on a Gallenkamp melting point apparatus and are uncorrected. Mass spectra were obtained a SHIMADZU QP 1100EX. IR spectra were recorded with a MATTSON 1000 FT-IR spectrophotometer. Nuclear magnetic resonance spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer using tetramethylsilan (TMS) as an internal standard. All the reactions were carried out is an unmodified domestic microwave oven BC380W having a maximum output of 900W operating at 2450MHz.

Activation of zeolite: This means that we leached zeolite with 8M NH3 solution for 48h then filtrated and heated in the oven at 400°C.

2-Phenyl-5(4H)-oxazolone derivatives MW method: Appropriate aldehyde or ketone (0.01 mol), hippuric acid (0.01 mol), zeolite (10g), were introduced into a beaker. Paste thus formed is irradiated in a microwave oven at a power output of 600w for an appropriate time. After irradiation, zeolite was ~~washed three times with dichloromethane and filtered. The filtrate was evaporated under reduced~~ pressure to give oxazolone which was recrystallized with ethanol 96% (using active carbon).

Thermal heating method: The appropriate aldehyde or ketone (0.01mol), hippuric acid (0.01mol), zeolite (10g) were introduced into a beaker. The mixture was heated for the appropriate time. Then zeolite was washed three times with dichloromethane and was filtered. The filtrate was evaporated under reduced pressure to give oxazolone, which was recrystallized with ethanol 96% (using active carbon). All the products obtained were characterized by IR, Mass spetra and 1H NMR spectroscopy and finally by comparison with authentic samples.

Conclusion

The replacement of toxic organic solvents is one of the most important goals in green chemistry, which inevitably lead to solvent emission and/or waste. The use of reagents supported on solid inorganic supports is an area currently under active investigation. These not only avoid the use of solvents for carrying out reactions but also induce significant simplification to the reaction procedures.

The use of microwave irradiation for carrying out organic reactions is clean, fast and economical. Coupling of the two techniques, that is, organic reaction using supported reagents with microwave irradiation has been a field, which has shown excellent results leading to the development of many reaction procedures, which are environmental friendly and falling in the domain of green chemistry.

One theory is that the origin of life on earth holds key to the organic molecules, which were transported to earth from interstellar space. Another argues that organics were produced by lightning storms in early earth s reducing atmosphere, eventually leading to a "primordial soup" in the ocean.

Now a report that amino acids can link up to form peptides under conditions like those at undersea volcanic vents bolsters support for a third theory, which holds that life on earth originated from reactions on the surfaces of minerals[15].

5(4H)-Oxazolones are intermediate for the synthesis of amino acids. Our approach confirms that life on earth originated from reactions on the surfaces of minerals.

References and notes

1. M. Novotna,V. Satava, A. Klouzkova, P. Kostka, D. Lezal, Journal of Optelectronic and Advanced Materials. **5**, 1405-1409 (2003).
2. G. Artioli, K. Stahl, G. Cruciani, A. Gualtieri, J.C. Hanson, American mineragolist. **86**, 185-192 (2001).
3. M. Rozic, S. Cerjan Stefanovic, L. Curkovich, Croatica chemical acta.**75**, 255-269 (2002).
4. T. Armbruster, A. Galarnau, F. Direnzo, F. Faujula, J. Vedrine.(eds), Zeolites and Mesoporous Material at the Dawn of the 21 st Century. 13 (2001).
5. E.M. Beccalli, F. Clerici, M.L. Gelmi, Tetrahedron. **55**, 781-786 (1999).
6. M.A. Mesaik, S. Rahat, M.K. Khan, Z.M. Choudhary, S. Murad, Z. Ismail, A. Rahman, Bio-Chemistry. **12**, 2049-2057 (2004).
7. H. Hamidian, A. Momeni, Asian journal of chemistry. **19**, 970-974 (2007).
8. H. Hamidian, A. Momeni, Hetrocycl. Commun.. **12** (1), 29 (2006).
9. S. Paul, P. Nanda, R. Gupta, A. Loupy, Tetrahedron Letters. **45**, 425-427 (2004).
10. M. Kidwai, Pure Appl. Chem. 73(1), 147-151 (2001).
11. N. Deka, A.M. Mariotte, A. Boumendjel, Green Chemistry. **3**, 263-264 (2001).
12. M. Crawford, W.T. Little, J. Chem. Soc. 729 (1959).
13. Y.S. Rao, J.Org.Chem. **41**(4), 722-725 (1976).
14. P. Kumar, H.D. Mishra, A.K. Mukerjee, Synthesis. 836-838 (1980).
15. G. Wachtershauser, C&EN News. April 14, 7 (1997).

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