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Rapid and Efficient Oxidation of Organcic Compounds in Microvave Condition with New Phase Transfer Oxidative Agent : CTAMABC

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Abstract

The chief features of the microwave reactions are the enhanced selectivity, much improved reaction rates, milder reaction conditions and formation of cleaner products. These reactions are an efficient and mild methodology for oxidation of some organic compound is described using cetyltrimethylammonium bromochromate (CTMABC) under microwave irradiation.

Introduction

Over recent years, chromium (VI) based oxidizing agents have been extensively worked on leading to the development of a good number of reagents. Some of which have become quite popular and performing well as oxidizing agents. Some of the important entries in the list of regents, are the Collins reagent, [1] chromium trioxide -3, 5-dimethyl-pyrazol complex, [2] pyridinium chlrochromate (PCC), [3] pyridinum dichromate (PDC)[4] and 2,2'-bipyridinum chlorochromate (BiPCC). [5] The versatility of pyridinum fluorochromate (PFC), [6] goes well to prove the point. However, the chromium based regents that have been developed so far have some limitations that cannot be over looked. These include the inherent problems of acidity of the regents and their limited solubility in organic solvents. These regents have proved to be unsuitable for oxidations on several occasions. Consequently, the search for a prominent new reagent persisted which has now lead to the synthesis of cetyltrimethylammonium bromochromate (VI) $[CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3]\ [CrO_3\overset{-}{Br}]$. [7]

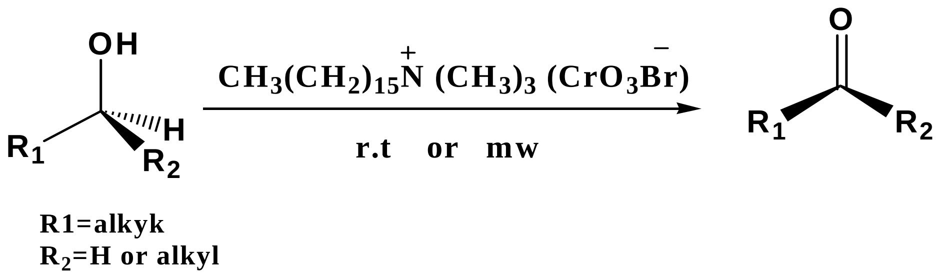
Results

The chief features of the microwave reactions are the enhanced selectivity, much improved reaction rates, milder reaction conditions and formation of cleaner products.[14] these reactions are especially appealing as they can be carried out in open vessels thus avoiding the risk of development of high pressures in addition to the associated case of manipulation.

Microwave techniques have become more effective than conventionally conducted reactions. Moreover, in a number of applications, reactions under microwave conditions can provide pure products in high yield.

There were primary incentives for selection of $[CH_3(CH_2)_{15}\ \overset{+}{N}\ (CH_3)_3]$ as the counter ion : quaternary ammonium ions are used as crystals growing agents.

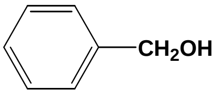
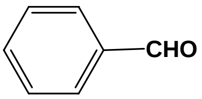
This work provides a useful new oxidant for organic chemists. The chemistry of CTMABC has been explored as an oxidizing agent (Scheme 1, Table 1).

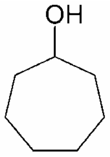
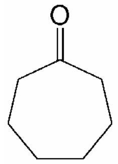
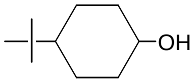
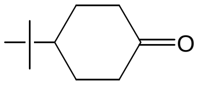
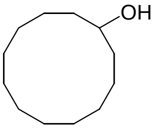
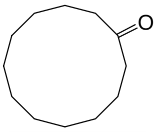
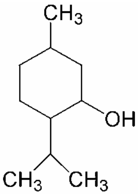
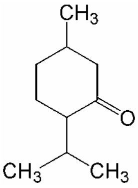
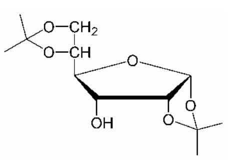
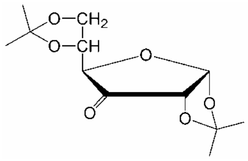
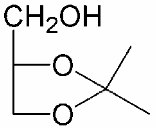
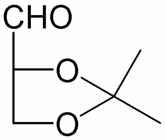


Scheme 1

Table 1: oxidation of some organic compounds with CTMABC, in solution and solution under microwave irradiation.

* the oxidant/substrate ratio in the case of compounds (8, 9, 10) in solution are 2/1.

	Substrate	Solution			Solution under Microwave	
		Time (min)	**Product**	**Yield (%)**	**Time (min)**	**Yield (%)**
1	$CH_3(CH_2)_4CH_2OH$	82	$CH_3(CH_2)_4$-CHO	85	8	95
2	$CH_3(CH_2)_6CH_2OH$	70	$CH_3(CH_2)_6$-CHO	87	13	92
3	$CH_3(CH_2)_9CH_2OH$	58	$CH_3(CH_2)_9$-CHO	88	11	90
4	 CH2OH	35	 CHO	90	5	98

5		65		90	14	95
6		400		78	10	83
7		40		84	15	89
*8		145		80	13	92
*9		60		80	15	85
*10		70		81	18	87

Because of the stability and solubility of CTMABC, reactions can be performed at room temperature and the separation of the Products is facile. During the reactions, the color of the oxidant changes from orange to brown, providing visual means for ascertaining the progress of the oxidation. The mechanism for the present oxidation is still unclear. However we assume that the mechanism of oxidation is similar to that of other bromochromates.[6] In addition, this oxidant and the oxidation conditions can be used for the synthesis of highly functionalized molecules.

Table 1, summarizes the products, yields and times of reaction of CTMABC with various substrates. The oxidative effect of CTMABC on polycyclic rings appears more pronounced than alcohols.[7] this could be due to the interaction of π - electrons with the quaternary cation as suggested by Felder [10]and Pullman[11].

The probable importance of such interactions in biological recognition processes has been emphasized by dugherty et al.[8] it has also been found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required , and especially in the short reaction times and in higher product yields (Table 1). [6, 7, 12, 13]

In conclusion, we have developed a mild, fast, and efficient method for the selective oxidation of aliphatic and benzylic alcohols to their corresponding carbonyl compounds by employing the microwave irradiation and magnetically retrievable oxidant.

The advantages of this protocol include a simple reaction set-up, application of commercially available reagents as well as oxidant. As we shown in the high product yields and short reaction times are the results of higher temperature of CTMAB during microwave experiments in comparison with conventional processes.

Oxidation of alcohols with cetyltrimethylammonium bromochromate (VI) (CTMAB) under microwave irradiation could be carried out much more quickly than using conventional techniques.(see Table 1)

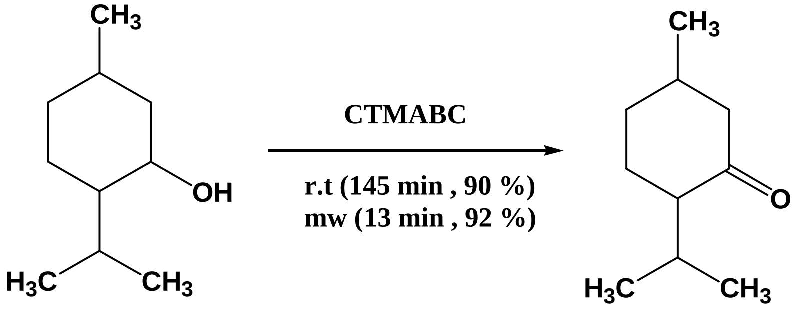
CTMAB as an oxidant is a very well suited reagent for microwave synthesis, because as an ionic and magnetically retrievable material, it carries a benefit conversion of electromagnetic energy into heat according to the dielectric heating mechanism.

In this paper, we reported a procedure where the oxidation was performed in microwave irradiation in order to improve the conditions and to prevent problems connected with conventional conditions (cost, handling, safety, pollution, and decreases in reactivity by dilution of the reactants).

cetyltrimethylammonium bromochromate (CTMAB) was prepared by the reported method.[7]

Microwave activation rather than conventional heating was preferred, as some solvent are rather poor thermal conductors (with consequently an important gradient in temperature inside the materials), whereas they behave as strong microwave absorbents (and therefore with a better homogeneity in temperature).[15] Consequently, reactions were generally faster and the obtained products more pure.[16]

The oxidations gave excellent yields within very short reaction times. For instance, the reaction time was reduced from 145 min to 13 min for oxidation of menthol into menthone (scheme 2).



Scheme 1

^{1}H NMR($CDCl_3$): 2.20(m, 1H, CH), 2.16 (d, 2H, CH_2), 2.05 (m, 1H, CH) , 1.95

(m,1H , CH) , 1.78 (m, 4H ,CH_2) , 1.06(d , 3H , CH_3) . 1(d, 6H, CH_3).

Discussion

Our method describes a noticeable improvement in reaction conditions for the selective oxidation of alcohols and takes advantage of both conventional method and microwave activation (under the same conditions of time and temperature, yields were reduced to 40-80 % by conventional heating.
Enhancement of chemical reaction as compared to conventional chemistry can manifest in several ways including the following: 1) highly accelerated reaction rates for various types of reactions. 2) Improved yield in many cases. 3) Reduction in side products. 4) Limited amounts of solvents needed as reaction media. 5) Successful product formation In some reactions that fail under conventional conditions and 6) simplification and improvement of classical synthetic methods.

Experimental

The reagent cetyltrimethylammonium bromochromate (VI) , $CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3[CrO_3Br^-]$ (CTMABC) , can be easily prepared in excellent yield from the reaction of CrO_3 with cetyltrimethylammonium bromide (CTMAB) in dry acetonitrile in the molar ratio of 1:1 that had been similar to described in the paper that published with us [8].
Microwave assisted rapid organic reactions constitute an emerging technology that could make industrially important organic synthesis more eco-friendly than conventional reactions.
In order to examine the oxidative ability of CTMABC, the following typical procedure was employed:

Typical procedure

Convenient method

To a stirred suspension of CTMABC (2.5 g) in dichloromethane (generally5 ml), a solution of the substrate in the minimum amount of dichloromethane is added drop wise, the molar ratio of oxidant to the substrate being 1:1(in the case of compounds 1- 7) or 2/1 (in the case of compounds 8- 10) (see Table 1). The mixture is refluxed for the time indicated in the table 1.[The completion of the reaction is followed by UV/vis and thin-layer chromatography (TLC) using ether/petroleum ether (60/40) as eluant.] The mixture is diluted with ether (1:1 vol/vol) and filtered through a short column of silica gel to give a clear solution. The solution is evaporated, and the residual product is purified by distillation, recrystallization, or column chromatography (Table 1). All boiling and melting points of oxidized compounds are according to the literature.[7,8] The progress of the reactions was monitored by uv/vis spectrophotometry. The amount of the oxidant during the reaction was measured spectrophotometrically at 350 nm. [7] Oxidation reaction progress shows that absorption of CTMABC decreases during the reaction progress. Spectrophotometric measurements were performed on a UV/visi Uvicon 922 spectrophotometer using thermostated matched 10-mm quartz cell. A very small magnetic stirrer was designed at the cell compartment in the bottom of sample cell in the spectrophotometer to stir up the solution in cell. The reaction mixtures remain homogenous in the solvent system used.

Microwave irradiation method

In a small scale experiment CTMABC (1 mmole) was suspended in acetonitrile (*ca.* 2 ml) and an alcohol (l mmole in 0.5 to1.5 ml of acetonitrile) was rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time. The mixture was irradiated for the time indicated in the table by microwave radiation (3.67 GHz, 300W) (table 1). The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progresses of the reactions were monitored by tlc and uv/vis spectrophotometer (at 352 nm). Analysis of the reaction mixture for the corresponding carbonyl compound was accomplished by the procedure reported in earlier papers. [7] All boiling and melting points of oxidized compounds are according to the literature.[7,8] The above procedure may be carried out on 1-100 g scales without any problem.

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