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Heptavalent Manganese Triggered Oxidation of Menthol and Camphor in Aqueous Sodium Bisulfate and organized Media using Micelles and Polyethylene Glycols

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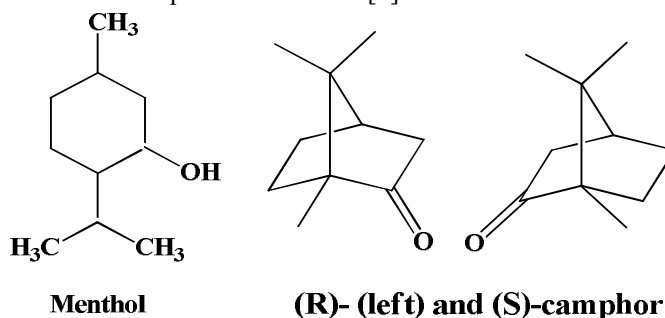
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Abstract: Permanganate oxidation of camphor, and menthol were studied in aqueous NaHSO₄ under different conditions. The reactions afforded menthone and camphoric acid respectively. The reactions underwent substantial rate acceleration in aqueous PEG and micellar media containing NaHSO₄. Highly significant rate enhancements are observed in ultrasonically assisted reactions, which were attributed to cavitation effects. Present protocols have depicted several greenery features such as simple work-up, fast reaction times, high product yield, eco-friendly and readily available additives as catalysts.

Keywords: KMnO₄ oxidation, camphor, menthol, bisulfate medium, sonication, rate acceleration

I. INTRODUCTION

Terpenoids are a class of natural products which are basically extracted from plant materials, and used in herbal remedies due to their aromatic qualities. Terpenoids like camphor, and menthol are largely used as herbal medicines in Indian subcontinent. Both these compounds are waxy, and crystalline solid substances with clear or white in color. Both the compounds are solids at room temperature, but melt slightly above it. Menthol belongs to the family of monocyclic monoterpenoids, while camphor is a bicyclic monoterpenoid ketone [1-4]. In this part of the world, both of them are explored for the treatment common health problems like cold and cough as mild analgesic, and cold-sore ointments. Menthol is used as food additive and side dish in several areas of India, Pakistan, while camphor is used as a main item in temples and Indian households during worship. Apart from Camphor is also used as medicine, it is also used as a plasticizer for nitrocellulose. Terpenoids contribute unforgettable scent of eucalyptus, the flavors of cinnamon, cloves, and ginger, the yellow color in sunflowers, and the red color in tomatoes. Menthol is found in peppermint oil (*Mentha Piperita* L., *Limiaceae*), while camphor is available in Formosan Camphor tree (*Cinnamomum camphora* T. Nees & Ebermeier, *Lauraceae*). Natural camphor is a dextrorotatory ketone with a specific rotation of $[\alpha]_D^{+42^\circ}$.



Over the years, camphor has attracted quite significant attention of chemists, with several of the derived products finding ingenious application as chiral synthons for natural products. Earlier work from our research group revealed that camphor (CAMP) underwent electrophilic substitution reactions (bromination, thiocyanation, and nitration) very easily under acid-free conditions in presence of a variety of oxidizing catalysts such as N-Bromosuccinimide (NBS), N-Bromophthalimide (NBP), N-Bromoacetamide (NBA), trichloroisocyanuric acid (TCICA), ceric ammonium nitrate (CAN), and ammonium metavanadate (AMV) in presence suitable salt (KBr for bromination, NH₄SCN for thiocyanation). However, nitration occurred in presence of NaNO₂ and KHSO₄. Noteworthy

rate accelerations are recorded in ultrasonically assisted reactions, which were attributed to cavitation effects [5]. During the synthesis of nano-diamond film through non-conventional CVD process, Chakraborty's research group used camphor as precursor [6,7]. High purity carbon nanotubes (CNTs) were synthesized using camphor as precursor by Kumar and Ando through CVD technique [8]. Above mentioned protocols [5-8] are largely in accordance with the green-chemistry principles of Paul Anastas and John Warner [9]. These principles suggest to focusing attention on designing and executing eco-friendly reactions using environmentally safe, economically cheap reagents, safer solvents, which will prevent environmental pollutions. Recent reviews and publications on micellar catalysis revealed that micelles act as a kind of micro / nano reactors, which enhance the rate and selectivity of a variety of chemical and biochemical reactions. In addition, a close parallelism between enzymatic reactions and micellar reactions has been observed in several biochemical protocols, which attracted the attention of several synthetic organic chemists and biochemists [10 -12]. Interestingly, poly ethylene glycols (PEGs) are also explored as safer catalysts and reaction media by replacing the toxic solvents in organic synthesis, which also revealed rate accelerations and selectivity of several organic reactions. Poly ethylene glycols also satisfy both economic and environmental demands in accordance with green chemistry principles [13 -15]. For the past several years, our group has focused attention in the design and execution of synthetic and kinetic protocols using eco-friendly materials, micelle-forming surfactants, unconventional energy sources like microwave propagation and sonication. Dramatic rate accelerations followed by an increase in the product yield were observed in all these reactions [16-19]. It is well known that potassium permanganate (KMnO_4) is easily available oxidizing agent available in the laboratory desk top of undergraduate and precollege institutions, which is used in analytical chemistry as well as synthetic organic chemistry, which can be handled easily at work bench [20-22]. Encouraged by the striking features and applications of PEGs, micelles, and ultrasound in chemical processes and organic synthesis, coupled with zeal to employ atom economy eco-friendly reagents, the authors have taken up the present study comprising Mn(VII) triggered oxidation of menthol and camphor in aqueous sodium bisulfate and organized media using micelles and polyethylene glycols. The proposed work is taken up under sonication, in addition to conventional solvothermal methods.

II. EXPERIMENTAL DETAILS

A. Materials and Methods

All the chemicals used were of analytical grade. Doubly distilled water (distilled over alkaline KMnO_4 and acid dichromate in an all glass apparatus) was used whenever required. Acetonitrile and other solvents were HPLC grade and used as such throughout the work. Menthol(Menth), Camphor (Camp) were procured from Aldrich. Polyethylene glycols (PEGs- PEG -200, PEG -300, PEG -400 and PEG – 600), Triton-X 100(TX-100), sodium dodecyl sulfate (SDS), and cetyl trimethyl ammonium bromide (CTAB), potassium permanganate (KMnO_4), and sodium bisulfate (NaHSO_4), were purchased from Avra or SD-fine chemicals (India).

B. General Procedure for Oxidation Reactions

A neat mixture of terpenoid (menthol /camphor (50 mmol) dissolved in acetonitrile and 50 mmol Mn(VII) reagent (dissolved in 10 mmol of NaHSO_4) were placed in a 50 ml round bottomed flask (R.B. flask) and continuously stirred till the reaction is completed. Progress of the reaction is monitored by TLC.

After completion of the reaction, the contents were extracted with dichloromethane (2 X 25 ml) and washed with water (40 ml). The dichloromethane layer was separated and dried over MgSO_4 . After evaporation of the solvent, the residue was purified by flash column chromatography (SiO_2 , ethyl acetate–hexane 1:2) to afford the end product.

C. Experimental Procedure For PEG / Micelle Mediated Oxidation Reactions

A neat mixture of camphor (1.0 mmol) dissolved in acetonitrile, PEG / micelle forming surfactant and reagent (1.2 mmol) were placed in a 50ml R.B. flask and refluxed till the reaction is completed as ascertained by TLC. The reactions times significantly decreased in presence of PEG/ micelles.

After completion of the reaction, the contents were treated according the above procedure to pure product of oxidation, which was characterized as camphoric acid ($\text{C}_8\text{H}_{14}(\text{COOH})_2$). Camphoric acid is saturated dicarboxylic acid with the same number of carbon atoms as camphor, it suggests that keto group is present in one of ring and ring contain keto group is opened in the formation of camphoric acid.

It is a colorless, odorless, a crystalline powder with melting-point (180° to 186°). It gave a yellowish-brown precipitate with ferric chloride and a light blue precipitate with copper sulphate. It could be easily titrated with normal solution of potassium hydroxide.

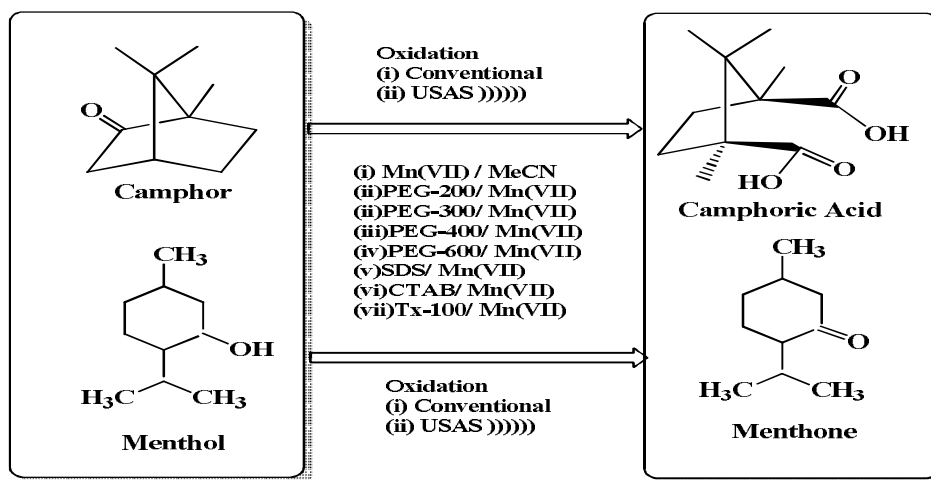
D. Experimental Procedure for Ultrasonically Assisted Oxidation Reactions

A neat mixture of terpenoid (menthol /camphor (50 mmol) dissolved in acetonitrile and 50 mmol Mn(VII) reagent (dissolved in 10 mmol of NaHSO₄) was placed in a 50 ml round bottomed flask (R.B. flask) and clamped in sonicator bath. Progress of the reaction is monitored by TLC. After completion of the reaction, the end product was obtained by the usual work-up described in the preceding sections.

In the case of camphor oxidation, main product of oxidation was characterized as chromotropic acid, as characterized by IR, NMR and Mass spectroscopic studies. Main product of oxidation was characterized as menthone. A portion of the isolated menthone was dissolved in suitable amount of acetonitrile and treated with an excess (200 mL) of a saturated solution of Brady's reagent (2,4-dinitrophenylhydrazine) in 2 mol/ dm³ acid and kept overnight in a refrigerator. The precipitated 2,4- dinitrophenyl hydrazone (DNP) was filtered, dried, weighed, recrystallized from ethanol. Obtained 2,4-DNP derivative was characterized by recording IR spectrum, which was in agreement with literature reports.

III. RESULTS & DISCUSSION

Oxidation reactions with camphor, and menthol were triggered by the addition of KMnO₄ aqueous NaHSO₄ solutions containing acetonitrile. The reactions afforded camphoric acid and menthone as reaction products. When the reactions are studied in presence of micelle forming surfactants (SDS, CTAB, Tx-100) and PEGs (PEG-200, PEG-300, PEG-400 and PEG-600), remarkable rate enhancements were observed as shown in the data presented in table-1. The rate enhancement in TX-100 micellar medium is on par with those in PEG media, probably because of structural similarities of PEGs and TX-100 due to the presence of poly-oxy ethylene moieties in their structures. Rate enhancements could be due to the hydrophobic interactions operating between the terpenoids and PEGs/Tx-100. However, anionic (SDS) and cationic (CTAB) micelle mediated reactions depicted relatively less effect over TX-100 (Table 1). Rate accelerations in micellar media could be attributed to the fact that micelles are known to act as micro to nano reactors.



Scheme 1: Mn(VII) triggered oxidation of Menthol and Camphor reactions under thermal conditions and Sonication

Another interesting feature in our studies is the accelerating effect of sonication on the rate of all substitution reactions observed in ultrasonically assisted reactions. The rate accelerations of the ultrasonically assisted could be due to cavitation phenomena, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid. Cavitation is a process in which mechanical activation destroys the attractive forces of molecules in the liquid phase. When the sample is subjected to sonication, ultrasound waves propagate into the liquid media resulting in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles in the liquid, which then collapse violently during compression, creating very high local temperatures in the liquid and enhance mass transfer. The reaction times under conventional stirred conditions reduced from several hours to about only few minutes in ultrasonically assisted condition. It is of interest to note that the results obtained in the present study are comparable with some of the earlier reports, which can be seen from the data presented in Table 1, indicating that the present work is also a sincere effort in the development of new eco-friendly protocols for substitution and oxidation reactions of camphor.

Table 1: Mn(VII) triggered oxidation of menthol and camphor in aqueous sodium bisulfate and organized media using micelles and polyethylene glycols

Terpenoid	Reagent (0.1-0.15mol)	Conventional		Sonication	
		Time (hr)	Yield (%)	Time (min)	Yield (%)
Camphor at 300-320K	Mn(VII)	3.5	70	60	80
	Mn(VII)-SDS	3.2	75	45	85
	Mn(VII)-CTAB	4.0	80	65	85
	Mn(VII)-Tx-100	2.5	76	40	81
	Mn(VII)-PEG-200	2.8	72	26	86
	Mn(VII)-PEG-300	3.8	77	53	88
	Mn(VII)-PEG-400	4.6	73	62	85
	Mn(VII)-PEG-600	5.1	76	74	82
Menthol at 300 K	Mn(VII)	4.5	80	60	80
	Mn(VII)-SDS	3.0	80	45	85
	Mn(VII)-CTAB	2.5	80	65	85
	Mn(VII)-Tx-100	2.0	76	40	81
	Mn(VII)-PEG-200	2.8	72	26	86
	Mn(VII)-PEG-300	3.8	77	53	88
	Mn(VII)-PEG-400	4.6	73	62	85
	Mn(VII)-PEG-600	5.1	76	74	82

IV. CONCLUSIONS

In summary, we have developed simple and efficient methods for Mn(VII) triggered oxidation of menthol and camphor in aqueous bisulfate and organized media using micelles and PEGs. Highly significant rate accelerations are recorded in ultrasonically assisted reactions, which were explained due to cavitation effects. On the other hand, the sluggish CAN oxidation of camphor underwent substantial rate acceleration in presence of PEGs and micelles. Present protocols have several advantages, such as simple work-up, fast reaction times, high product yield, eco-friendly and readily available additives as catalysts with experimental simplicity.

V. ACKNOWLEDGMENTS

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A. Statement for Conflict Interest

Authors declare that they do not have any conflict of interest.

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