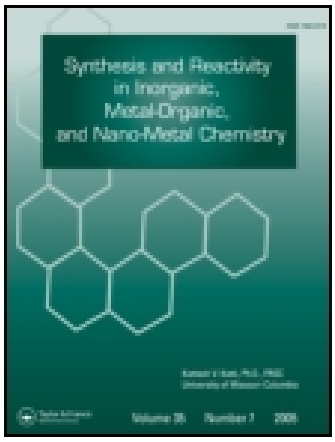


Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Efficient Selective Oxidation of Organic Substrates Using Pyridinum Sulfonate Halochromate Under Solvent-Free Conditions and Microwave Irradiation: Experimental and Theoretical Study

Ahmad R. Bekhradnia [a] & Sattar Arshadi [b]

[a] Pharmaceutical Sciences Research Center, Department of Medicinal Chemistry , Mazandaran University of Medical Sciences , Sari , I. R. Iran

[b] Department of Chemistry , Payame Noor University of Iran , Sari , I. R. Iran

Accepted author version posted online: 27 Mar 2012.Published online: 04 Jun 2012.

To cite this article: Ahmad R. Bekhradnia & Sattar Arshadi (2012) Efficient Selective Oxidation of Organic Substrates Using Pyridinum Sulfonate Halochromate Under Solvent-Free Conditions and Microwave Irradiation: Experimental and Theoretical Study, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:5, 705-710

To link to this article: http://dx.doi.org/10.1080/15533174.2011.615045

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:705–710, 2012

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2011.615045

Taylor & Francis
Taylor & Francis Group

Efficient Selective Oxidation of Organic Substrates Using Pyridinum Sulfonate Halochromate Under Solvent-Free Conditions and Microwave Irradiation: Experimental and Theoretical Study

Ahmad R. Bekhradnia[1] and Sattar Arshadi[2]

[1]*Pharmaceutical Sciences Research Center, Department of Medicinal Chemistry, Mazandaran University of Medical Sciences, Sari, I. R. Iran*

[2]*Department of Chemistry, Payame Noor University of Iran, Sari, I. R. Iran*

A convenient and rapid method has been developed for the selective oxidation of several types of alcohols to related carbonyl compounds under solvent-free conditions. In this study, the authors report the microwave-assisted selective oxidation of alcohols and a number of organic compounds with pyridinum sulfonate chlorochromate (PSCC) and pyridinum sulfonate fluorochromate (PSFC). The density functional theory calculations were made at B3LYP/6–31G* levels of theory and thermodynamic data supported the proposed mechanism involving formation of a halochromate ester, which showed that PSFC should be a more capable oxidant than PSCC. The oxidation products are easily obtained in short reaction time with good yields.

Keywords DFT calculations, oxidation mechanism, pyridinum sulfonate halochromate, selective oxidation, solvent-free conditions

INTRODUCTION

Over recent years, it has been an essential and challenging issue to develop an efficient method for selective oxidation of alcohols to the corresponding carbonyl compounds. To date, several general oxidations of alcohols have been reported, and the most classical oxidant among of them is hexavalent chromium.[1–5] Some of the most common oxidizing reagents are pyridinium chlorochromate,[6] pyridinum dichromate,[7] 2,2'-bipyridinium chlorochromate,[8] pyridinum fluorochromate (VI),[9] and Collins reagent.[10]

However, many important problems can occur during the oxidation process. Avoiding overoxidation, we have reported the reasonable and chemoselective oxidizing agents for the oxidation of alcohols and bioorganic substrates.[11,12] Nevertheless, the troublesome problem of oxidation with pyridinum sulfonate chlorochromate (PSCC) and pyridinum sulfonate fluorochromate (PSFC) was that organic solvent should be separated from the related carbonyl compound after the oxidation. Moreover, the high reaction time was attained when these reagents were employed. Therefore, we are going to report the microwave-assisted oxidation under solvent-free conditions with PSCC and PSFC. The use of microwave ovens for carrying out organic synthesis has attracted the attention of scientists over the last decades, which is due to the shorter reaction time, pure reactions, higher yields, superior selectivity, and lack of organic solvents in the reaction processes.[13–16] Herein, we wish to report an efficient procedure for the oxidation of the considered substrates with microwave and propose a mechanism which is supported by DFT calculation using the Gaussian 98 package.[17] Thermodynamic data were calculated at B3LYP/6–31G* levels of theory for PSFC and PSCC. These data included the sum of electronic and thermal energies (E), bond angles, bond distances, and Mulliken charges, which were obtained by the frequency option of Gaussian 98 program (Table 1).

EXPERIMENTAL

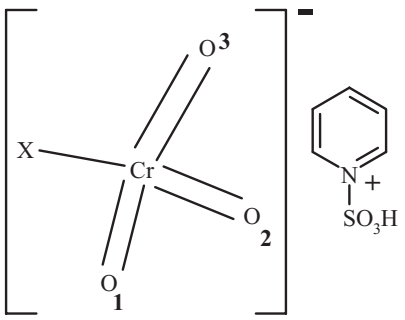
Preparation of the PSFC and PSCC reagents were made with pyridinium sulfonate fluoride and pyridinium sulfonate chloride as the starting materials, respectively. These compounds were prepared by adding fluorosulfonic acid as well as chlorosulfonic acid to pyridine in chloroform. At the result, the obtained pyridinium sulfonate halides were employed for synthesizing PSFC and PSCC reagents through the addition of chromium trioxide. The spectral data and elemental analysis are given subsequently:

Received 13 August 2011; accepted 13 August 2011.

The authors are pleased to acknowledge financial support from the Mazandaran University of Medical Sciences, "Professor's Project Funds." The authors wish to express their special thanks to Mrs. N. Khaki (Mazandaran University of Medical Sciences) for her editorial cooperation in completing this research.

Address correspondence to Ahmad R. Bekhradnia, Pharmaceutical Sciences Research Center, Department of Medicinal Chemistry, Mazandaran University of Medical Sciences, Sari 48175-861, I. R. Iran. E-mail: reza_bnia@yahoo.com

TABLE 1
Energies (E) (kcal/mol) along with the bond lengths, bond angles, and Mulliken charges for PSCC and PSFC, calculated by the DFT method



Entry	X=F	Bond lengths	Å	Bond angles	Degree		Charges	Energy (Kcal.mol-1)
1		**Cr-X**	1.792	O(3)-Cr-X	108.23	Cr	0.802887	−258.5
2		**Cr-O(1)**	1.614	O(2)-Cr-X	108.24	O(1)	−0.443592	
3		**Cr-O(2)**	1.614	O(1)-Cr-X	108.20	O(2)	−0.444075	
4		**Cr-O(3)**	1.614	O(3)-Cr-O(2)	110.68	O(3)	−0.444104	
5				O(3)-Cr-O(1)	110.68	X	−0.471117	
6				O(2)-Cr-O(1)	110.69			
7	**X=Cl**	**Cr-X**	2.275	O(3)-Cr-X	107.76	Cr	0.620281	−205.2
8		Cr-O(1)	1.610	O(2)-Cr-X	107.73	O(1)	−0.416549	
9		Cr-O(2)	1.610	O(1)-Cr-X	107.76	O(2)	−0.416539	
10		Cr-O(3)	1.609	O(3)-Cr-O(2)	111.11	O(3)	−0.416556	
11				O(3)-Cr-O(1)	111.11	X	−0.370637	
12				O(2)-Cr-O(1)	111.14			

PSFC: ^{1}H NMR (90 MHz, CH_3CN): $\delta = 8.1$ (m, 2H, *m*-CH), 8.7 (m, 1H, *p*-CH), 8.9 (m, 2H, *o*-CH), ^{13}C NMR (22.5 MHz, CH_3CN): $\delta = 129.5$ (2C, *m*-CH), 148.5 (1C, *p*-CH), 181.5 (2C, *o*-CH); IR ν(KBr): 953 (s, Cr-O), 916 (s, Cr-O), 630 (m, Cr-F), 1150–1250 (s, SO3) 1450–1650 cm^{-1} (originating due to the pyridinium sulfonate cation); UV(CH_3CN): 329–428 (Cr-F), 255 and 288 nm (originating due to the pyridinium sulfonate cation). Elemental analysis data for the PSFC is the following: Cr, 17.93%; C, 21.53%; N, 5.07%; H, 1.93%. Anal. Calcd.: Cr, 17.65%; F, 6.81%; C, 21.50%; N, 5.01%; H, 2.15%.

PSCC: ^{1}H NMR (90 MHz, CH_3CN): $\delta = 7.9$ (m, 2H, *m*-CH), 8.4 (m, 1H, *p*-CH), 8.6 (m, 2H, *o*-CH), ^{13}C NMR (22.5 MHz, CH_3CN): $\delta = 125.3$ (2C, *m*-CH), 139.2 (1C, *p*-CH), 176.9 (2C, *o*-CH); IR ν(KBr): 958 (s, Cr-O), 924 (s, Cr-O), 610 (m, Cr-Cl), 1120–1250 (s, SO3) 1420–1630 cm^{-1} (originating due to the pyridinium sulfonate cation); UV(CH_3CN): 350–400 (Cr-Cl), 256 and 260 nm (originating due to the pyridinium sulfonate cation). Elemental analysis data for the PSCC is the following: Cr, 17.60%; C, 20.46%; N, 4.80%; H, 1.88%. Anal. Calcd.: Cr, 17.65%; C, 20.38%; N, 4.75%; H, 1.83%.

General Procedure for the Application of PSFC and PSCC in Solvent-Free Conditions as the Oxidizing Agents

The solid organic substrates were added in a mortar until they became homogeneous by the addition of oxidant with the molar ratios of 1:1.1 (entries 1–19) to 1:5 (entries 20–21). The reaction mixture was placed in a 100 mL, three-necked, round-bottomed flask, completed with Teflon-coated magnetic stirring bar and fiber-optic temperature sensor; the magnetic stirrer was set at 80% of the maximum speed, and the reaction mixture was treated for the time indicated in Table 2 at 300/500 W. The completion of the reaction oxidations was scrutinized by UV-vis spectrometer. After the completion of the reaction, the extent of the oxidation was determined with proton nuclear magnetic resonance (^{1}H NMR) (Table 2). The spectral data of products, ^{1}H-NMR (90 MHz, $CDCl_3$, δ/ppm); ^{13}C NMR (22.5 MHz, CDCl3, δ/ppm) are the following:

Product (1): ^{1}H-NMR*:* 7.6 (m, 2H, *m*-CH), 7.8 (m, 2H, *o*-CH), 9.8 (s, 1H, -CHO); ^{13}C-NMR: 130.1 (C-Br), 132.1 (2C,

TABLE 2
Oxidation of organic substrates with PSFC and PSCC under microwave irradiation conditions

Entry	Compound	Time (sec) PSFC	Time (sec) PSCC	Substrate: oxidant	Product	Yield
1	4-Bromobenzyl alcohol	30	40	1:1.1	4-Bromobenzaldehyde	80%
2	4-Methylbenzyl alcohol	15	15	1:1.1	4-Methylbenzaldehyde	86%
3	Ethyl alcohol	30	40	1:1.4	Acetaldehyde	89%
4	4-Methoxybenzyl alcohol	10	15	1:1.1	4-Methoxybenzaldehyde	96%
5	Benzyl alcohol	15	15	1:1.1	Benzaldehyde	95%
6	1-Pentanol	35	45	1:1.4	1-Pentanal	86%
7	2,6-Dimethylcyclohexanol	40	55	1:1.3	2,6-Dimethylcyclohexanone	77%
8	Methanol	35	50	1:1.4	Formaldehyde	84%
9	2-Methyl-1-propanol	35	55	1:1.4	2-Methylpropanal	89%
10	Cyclohexanol	35	45	1:1.4	Cyclohexanone	80%
11	1-Butanol	45	60	1:1.4	1-Butanal	89%
12	Allyl alcohol	25	30	1:1.1	Acrolein	95%
13	3-Chloro-2-butene-1-ol	40	50	1:1.2	3-Chloro-2-butenal	76%
14	Furfuryl alcohol	35	50	1:1.2	Furfural	81%
15	Ethylene glycol	35	55	1:1.3	Glyoxal	80%
16	Cinnamyl alcohol	30	30	1:1.2	Cinnamaldehyde	84%
17	Anthracene	20	40	1:1.3	Anthraquinone	80%
18	Phenanthrene	100	100	1:1.2	9,10-Phenanthrenequinone	81%
19	1,8-Dihyroxy-9(10H) anthracenones	80	80	1:1.5	1, 8-Dihydroxy- 9, 10-antracenedione	88%
20	Cholest-5-en-3-ol benzoate	400	400	1:5	7-Keto-cholest-5-en-3-ol benzoate	82%
21	Cholest-5-en-3-ol acetate	400	400	1:5	7-Keto-cholest-5-en-3-ol acetate	87%

m-CH), 131.2 (2C, *o*-CH), 134.8 (1C,C-CHO), 185.7 (-CHO).

Product (2): ^{1}H-NMR*:* 2.4 (s, 3H, -OCH_3), 7.5 (m, 2H, *m*-CH), 7.8 (m, 2H, *0*-CH), 9.8 (s, 1H, -CHO); ^{13}C-NMR: 22.9 (-CH_3) 128.1 (4C, -CH), 134.9 (1C,C-CHO), 145.1 (1C−CH_3), 189.2 (-CHO).

Product (3): ^{1}H-NMR*:* 2.3 (s, 3H, -CH_3), 9.4 (s, 1H, -CHO); ^{13}C-NMR: 32.1 (1C−CH_3) 197.2 (1C–CHO).

Product (4): ^{1}H-NMR*:* 3.8 (s, 3H, -OCH_3), 6.8 (m, 2H, *m*-CH), 7.8 (m, 2H, *0*-CH), 9.8 (s, 1H, -CHO); ^{13}C-NMR: 58.9 (-OCH_3) 116.1 (2C, *m*-CH), 129.2 (1C,C-CHO), 131.2 (2C, *o*-CH), 165.1 (C-O CH_3), 186.2 (-CHO).

Product (5): ^{1}H-NMR*:* 7.4–7.9 (m, 5H, -ph), 9.8 (s, 1H, -CHO); ^{13}C-NMR: 128.5–137.5 (*5c*-ph), 189.9 (-CHO).

Product (6): ^{1}H-NMR*:* 0.9 (*t*, 3H, -CH_3), 1.3–1.5 (m, 4H, −CH_2), 2.3 (t, 2H, CH_2), 9.0 (s, 1H, -CHO); ^{13}C-NMR:14.9 (1C-CH_3), 23.1 (1C-CH_2), 24.2 (1C-CH_2), 44.1 (1C-CH_2), 199.6 (-CHO).

Product (7): ^{1}H-NMR*:* 1.2 (*d*, 6H, -CH_3), 1.6 (m, 6H, −CH_2), 2.2 (m, 2H, CH); ^{13}C-NMR: 17.8 (6C-CH_3), 21.1 (1C-CH_2), 33.3 (2C-CH_2), 42.1 (2C-CH), 209.9 (−C=O).

Product (8): ^{1}H-NMR*:* 9.2; ^{13}C-NMR: 182.1.

Product (9): ^{1}H-NMR: 1.0 (d, 6H, -CH3), 2.3 (m, 1H, -CH), 9.2 (s, 1H, CHO); 13C-NMR: 13.4 (2C,-CH3), 39.4(1C,-CH), 199.2 (1C, -CHO).

Product (10): ^{1}H-NMR: 1.5–1.8 (10H, −CH_2); ^{13}C-NMR: 21.3 (1C,−CH_2), 26.1(2C,−CH_2), 39.6 (2C,-CH), 201.5 (1C, −C=O).

Product (11): ^{1}H-NMR: 1.0 (t, 3H, −CH_3), 1.5 (m, 2H, −CH_2), 2.2 (t, 2H, −CH_2), 9.2 (s,1H,-CHO); ^{13}C-NMR: 13.4 (1C,−CH_3), 14.5(1C,−CH_2), 43.7(1C,−CH_2), 196.4 (1C, -CHO).

Product (12): ^{1}H-NMR: 5.9 (dd, 1H, −CH_2), 6.2 (m, 1H, −CH_2), 6.3 (dd, 1H, -CH), 9.1 (s,-CHO); ^{13}C-NMR: 23.8 (1C,−CH_3), 129.5 (1C,−CH_2), 133.6 (1C,-CH), 190.5 (1C, −C=O).

Product (13): ^{1}H-NMR: 2.3 (s, 3H, −CH_3), 6.0 (s, 1H, -CHCl), 9.3 (s, 1H, -CHO); ^{13}C-NMR: 24.3 (1C,−CH_3), 128.5 (1C, = CH), 149.2 (1C, = CCl), 181.2 (1C, -CHO).

Product (14): ^{1}H-NMR: 6.2 (dd, 1H, = CH), 6.8 (d, 1H, = CH), 7.2 (d, 1H, = CH), 9.2 (s, CHO); ^{13}C-NMR: 109.3 (1C, = CH), 118.1 (1C, = CH), 141.1 (1C, = CH), 149.4 (1C, = C-O), 171.2 (1C, -CHO).

Product (15): ^{1}H-NMR: 9.6 (s, 2H, -CHO); ^{13}C-NMR: 180.5 (2C,-CHO).

Product (16): ^{1}H-NMR: 6.3 (d, 1H, = CH), 7.0–7.2 (5H, Ar-H), 7.4 (d, 1H, = CH), 9.1 (s, 1H, -CHO); ^{13}C-NMR: 123.9–130.1 (Ar-CH), 128.9 (1C, = CH), 149.1 (1C, = CH), 189.2 (1C, CHO).

Product (17): ^{1}H-NMR: 7.7–8.1 (Ar = CH); ^{13}C-NMR: 122.9 and 132.1 (Ar-CH), 131.1 (Ar-C), 181.1 (2C, C=O).

Product (18): ^{1}H-NMR: 7.1 (m, 2H, Ar-H), 7.3 (m,2H, Ar-H), 7.6 (m, 2H, Ar-H), 7.9 (m, 2H, Ar-H); ^{13}C-NMR: 121.2 (2C, Ar-CH), 124.9 (2C, Ar-C), 126.1 (2C, Ar-CH), 129.2 (2C, Ar-CH), 130.3 (2C, Ar-C), 133.1 (2C, Ar-CH), 178.1 (2C, C=O).

Product (19): ^{1}H-NMR: 7.1 (dd, 2H, Ar-H), 7.5 (dd,2H, Ar-H), 7.6 (dd, 2H, Ar-H), 11.5 (2H, Ar-OH); ^{13}C-NMR: 114.2 (2C, Ar-C), 117.6 (2C, Ar-CH), 121.3 (2C, Ar-CH), 130.8 (2C, Ar-C), 134.9 (2C,Ar-CH), 157.8 (2C, Ar-CHOH), 177.1 (Ar-CO), 186.3 (Ar-CO).

Product (20): ^{1}H-NMR: 1.8 (dd, 1H, HC-CO-), 2.1 (m, 2H, −CH2), 2.3 (d, 2H, $-CH_2$), 3.9(m, 1H, −CH−O−), 5.3 (s, CH = C), 7.5–8.1 (5H, Ar-H); ^{13}C-NMR: 32.1 (1C, −CH2), 43.2 (1C, −CH2), 73.4 (1C, CH−O), 126.7 (1C, = CH-), 162.3 (1C, −C=), 200.4 (−O−CO benzoate), 167.9 (C=O).

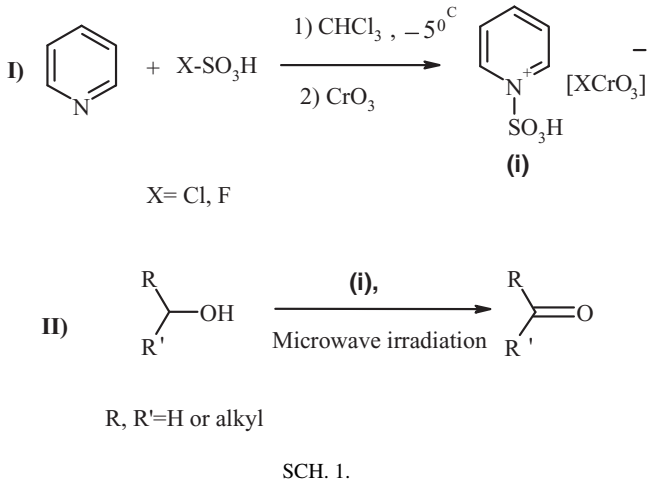
Product (21): ^{1}H-NMR: 1.6 (dd, 1H, HC-CO-), 1.8 (m, 2H, −CH2), 2.0 (s, 3H, $CO-CH_3$), 2.2 (d, 2H, $-CH_2$), 4.5 (m, 1H, −CH−O−), 5.8 (s, CH = C); ^{13}C-NMR: 21.2 (1C, O-CH3 Acetyl), 27.3 (1C, −CH2), 37.3 (1C, −CH2), 70.8 (1C, CH−O), 125.9 (1C, = CH-), 161.1 (1C, −C=), 171.4 (−O−CO Acetyl), 191.2 (C=O).

Geometry optimizations were performed in Pharmaceutical Sciences Research Center, Sari, using the Gaussian 98 system of programs.[17] To assess the performance of this approach, the compounds were computed at higher theoretical levels, in a way that HF/STO-3G outputs were used as inputs for the HF/6–31G*. Also, HF/6–31G* outputs were used as inputs for the B3LYP/6–31G*. The latter method was preferred because it was less common to find any significant spin contamination in DFT calculations.

RESULTS AND DISCUSSION

All microwave irradiation reactions were carried out on a Milestone Micro-SYNTH apparatus (Mazandaran University of Medical Sciences). Internal temperatures were measured with fiber-optic sensor in conjunction with Milestone immersion well.

^{1}H spectra and ^{13}C NMR were recorded using a JEOL JNM-EX90A spectrometer (Tarbiat Modares University). Chemical shifts (δ) are given in ppm relative to TMS. The UV-vis spectra were obtained using a Perkin-Elmer lambda-EZ 201 spectrometer (Mazandaran University of Medical Sciences). Melting point was measured in open capillary tubes with an Electrothermal-9200 melting point apparatus (Mazandaran University of Medical Sciences).

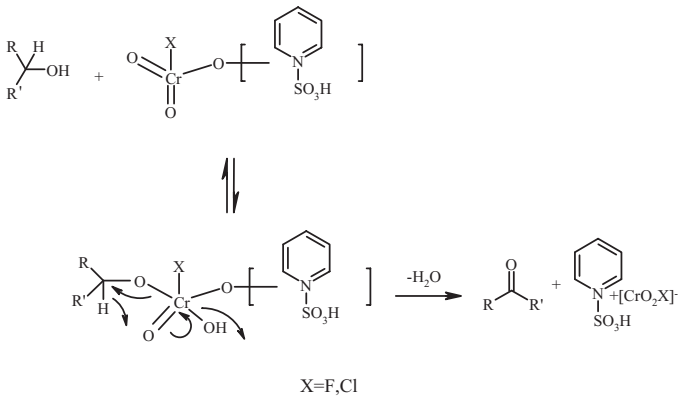


SCH. 1.

The synthesis of reagents PSFC and PSCC were accomplished, as before.[11,12] First, pyridinium sulfonate fluoride and pyridinium sulfonate chloride were prepared by adding fluorosulfonic acid and chlorosulfonic acid to pyridine in chloroform, respectively. Consequently, these prepared compounds were employed for synthesizing PSFC and PSCC reagents through addition of chrome trioxide (CrO_3) (Scheme 1).

To scrutinize reaction conditions, several alcohols and other bio-organic compounds were employed and oxidized under microwave irradiation. The aptitude of a specific substance to convert electromagnetic energy into heat is known as loss tangent, tan δ. A reaction with a high tan δ is required for efficient absorption and consequently rapid heating. However, the compounds with high dielectric constant cannot necessarily have high tan δ values. Actually, alcohols and most of organic compounds have a considerably lower dielectric constant, but heat much rapidly in a microwave field due to their high tan δ. All used compounds as substrates had high tan δ microwave-absorbing.[18]

Different alcohols and bioorganic compounds, with high tan δ, in various conditions were investigated until we obtained good isolated yields of related products (Table 2). The substrate: oxidant molar ratios of 1:1.1 to 1:1.5 for entries 1–19 as well as 1:5 for entries 20–21 were employed. Microwave-assisted oxidation of primary, secondary, allylic, and benzylic alcohols resulted in a better yield compared with solvent conditions (entries 1–13 in Table 2). Microwave irradiation also permitted a shorter reaction time for both PSCC and PSFC. Moreover, various biological compounds can be prepared by this method. For example, cholest-5-en-3-ol acetate and cholest-5-en-3-ol benzoate were chemoselectively oxidized at position 7 in solvent-free conditions (entries 20 and 21 in Table 2). For the mentioned bioorganic compounds, the reaction time of microwave-assisted oxidation for both PSFC and PSCC was much shorter than that of solvent conditions and also both led to good yields. These derivatives are found in mammal tissues and are known in cell replication process.[19,20]



SCH. 2. The proposed oxidation mechanism by PSCC and PSFC supported by the DFT method.

In addition to what is mentioned, 1,8-dihyroxy-9(10H) anthracenones derivatives with blocked position 10 are known as compounds having substantial therapeutic activity and minimal inflammatory effect.[21] In solvent-free conditions, 1,8-dihydroxy-9,10-anthracenedione was afforded by PSFC and PSCC oxidants (1:1.5, substrate:oxidant) in excellent yield and short reaction time (entry 19, Table 2).

Analysis of brown residue remaining after the oxidation reaction was accomplished by the procedure reported in a previous paper.[12] The magnetic susceptibility was measured to the amount of 2.88 BM at room temperature. Thus, the oxidation level of the metal was 3.8–4.1. This confirmed that the isolated solid product was $C_5H_5NSO_3H$ [CrO_2X], where X=F, Cl.

Based on the oxidation level of the residue, the proposed mechanism can be involved in the formation of a halochromate ester that leads to a conversion in the following step to the related carbonyl compounds (Scheme 2).

The theoretical study of the PSFC and PSCC structures were performed by DFT method (Table 1). The Mulliken charge of chromium atom in PSFC (entry 1, Table 1) was more than that of PSCC (entry 7, Table 1). Therefore, these calculations support our proposed mechanism (Scheme 2) and show the chromium atom of PSFC is more capable oxidant than that of PSCC.

Thus, the fluorine atom in PSFC contributes to oxygen transfer oxidations more rapidly than chlorine atom in PSCC reagent. Hence, the proposed intermediate halochromate anion is easily converted to Cr(IV) species. Moreover, the reaction time of oxidations with PSFC is much shorter than that of PSCC oxidant for similar substrates and it results in better yields.

Noticeably, due to reaction conditions, the completion of reaction could not be evaluated with thin layer chromatography (TLC). The application of TLC solvents may result in the complication in oxidation products and circumstances. To avoid such complications, the progress of the reaction was investigated by UV-vis spectrometer. The maximum absorbance was found at $\lambda = 329–430$ nm for (Cr–F) in PSFC and at $\lambda = 250–400$ nm for (Cr–Cl) in PSCC reagents. These absorption bands are related to ligand-to-metal charge transfer (LMCT) with highly intense and lie in the ultraviolet or visible portion of the spectrum. LMCT complex arises from transfer of electrons from molecular orbital of oxygen, as ligand-like character, to that chromium as metal-like character. This type of transfer is done if the chromium has low-lying empty orbitals. The PSCC and PSFC reagents have chromium in high oxidation state, Cr (VI). After the completion of the oxidation reaction, the chromium was reduced to Cr (IV) as residue product, which was a complex compound of Cr (IV), $C_5H_5NSO_3H$ [CrO_2F].[11] Apparently, the transition energies correlated with the order of oxidation number. Therefore, the chromium molecular orbital energy increased with the progress of oxidation reaction and LMCT spectral band position in the absorption shifted to a shorter wavelength (hypsochromic shift). Thus, the UV-vis spectroscopy is an efficient method for evaluation of progress of oxidation reaction in solvent-free conditions.

CONCLUSIONS

The advantages in the use of this method are shorter reaction time, higher yields, economical technology, lack of solvent use, and waste generation. Moreover, the oxidation of these compounds is performed devoid of overoxidation during the reaction process. A variety of functionalities are investigated in these solvent-free conditions and the selective products have been obtained in excellent overall yields. This procedure provides an ideal synthetic approach for carbonyl and some biological compounds. Furthermore, on the basis of our DFT calculations and proposed oxidation mechanism, PSFC is suggested to be a more capable oxidant reagent than PSCC. However, due to the limited capacity of our current microwave equipment, these reactions have not been carried out on a larger scale. However, it was supposed that the present method should be simply extended to large-scale syntheses when appropriate microwave apparatus and efficient separation method are used.

REFERENCES

1. Freeman, F. In *Organic Synthesis by Oxidation with Metal Compounds*; Plenum Press: New York, **1986**; p. 68.
2. Regen, S.; Koteel, C. *J. Am. Chem. Soc*. **1977**, *99*, 3837.
3. Tang, J.; Zhu, J.; Shen, Z.; Zhang, Y. *Tetrahedron Lett*. **2007**, *48*, 1919.
4. Ley, S. V.; Madin, A. In *Comprehensive Organic Synthesis*; eds. B. M. Trost, I. Fleming; Pergamon Press: London, **1991**; Vol. 7, pp. 251–289.
5. Meenakshisundaram, S.; Markkandan, R. *Trans. Met. Chem.* **2004**, *29*, 136.
6. Corey, E.; Suggs, J. *Tetrahedron Lett*. **1975**, *16*, 2647.
7. Corey, E.; Schmidt, G. *Tetrahedron Lett*. **1979**, *20*, 399.
8. Guziece, F.; Luzzio, F. *Synthesis* **1980**, 691.
9. Bhattacherjee, M.; Chaudhuri, M.; Purkayastha, S. *Tetrahedron* **1987**, *43*, 538.
10. Collins, J.; Hes, W.; Frank, F. *Tetrahedron Lett.* **1968**, *9*, 3363.
11. Bekhradnia, A .R.; Zahir, F.; Arshadi, S. *Monatsh Chem*. **2008**, *139*, 521.
12. Kassaee, M. Z.; Bekhradnia, A. R. *Phosphorus Sulfur* **2004**, *179*, 2025.

13. Dallinger, D.; Kappe, C. *Chem. Rev*. **2007**, *107*, 2563.
14. Kappe, C. *Angew. Chem.* Int. *Ed.* **2004**, *43*, 6250.
15. Stadler, A.; Pichler, S.; Horeis, G.; Kappe, C. *Tetrahedron* **2002**, *58*, 3177.
16. Kidwai, M. *Pure App. Chem.* **2001**, *73*, 147.
17. (a) Bekhradnia, A. R.; Ebrahimzadeh, M. A.; Hejazi, V.; Gorji, R.; Vessally, E. *Asian J. Chem.* **2009**, *21*, 2110; (b) Bekhradnia, A. R.; Arshadi, S. *Chin. J. Struct. Chem* **2011**, *30*, 906; (c) Arshadi, S.; Bekhradnia, A. R.; Ahmadi, S.; Karami, A. R.; Pourbeyram, S. *Chin. J. Chem.* **2011**, *29* (7), 1347; (d) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Znkrzewski,V.G.; Montgomery, G.A.; Startmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A. D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pamelli, C.; Adamo, G.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokoma, K.; Malick, D.K.; Rubuck, A. D.; Raghavachari, K.; Foresman, J.B.; Cioslawski, J.; Oritz, J.V.; Stlefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Comperts, R.; Martin, R.L.; Fox, P.J.; Keith, T.; Al-laham, M.A.; Peng, C.Y.; Akkara, A.N.; Gonzales, C. G.; Combe, M.C.; Gill, P.M.W.; Johnson, B.; Chem, W.; Wong, M.W.; Andres, J.L.; Gonzales, C.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A. Gaussian Inc.: Pittsburgh, PA, **1998**.
18. Hayes, B.L. *Microwave Synthesis: Chemistry at the speed of light*; CEM: Matthews, NC, **2002**.
19. Kassaee, M. Z.; Bekhradnia, A. R. J. *Biosci. Bioeng,.* **2003**, *95*, 526; (b) Schroepfer, G. J. *Ann. Rev. Biochem.* **1981**, *51*, 585.
20. Taylor, F.R.; Saucier, S.E.; Shown, E.P.; Parish, E.J.; Kandutsch, A.A. *J. Biol. Chem*. **1984**, *259*, 12382.
21. Wilson, C.O.; Gisvold, O. *Textbook of Organic Medicinal and Pharmaceutical Chemistry*; New York: Lippincott-Raven, **1998**.