

MILD, EFFICIENT OXIDATION OF ALCOHOLS TO ALDEHYDES AND KETONES WITH PERIODIC ACID CATALYZED BY SYM-COLLIDINIUM CHLOROCHROMATE (S-COCC) AND DFT STUDIES, HOMO–LUMO AND MEPS MAPPINGS OF PRODUCTS

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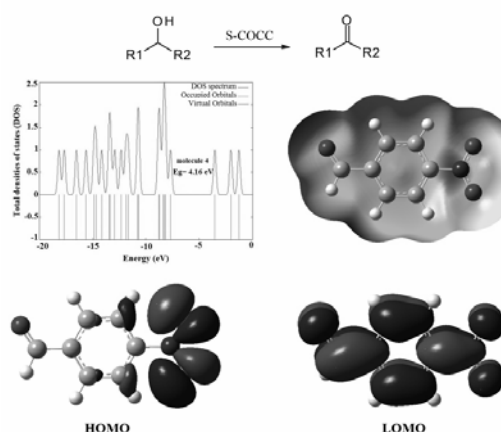
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A facile sym-collidinium chlorochromate (S-COCC) catalyzed (2 mol%) oxidations of alcohols to aldehydes or ketones using 1 equiv of H5IO6 as oxidant in acetonitril at room temperature with excellent yields is described. A mild and efficient method has been optimized for S-COCC catalyst by considering the effect of various parameters such as the reaction time, the amount of catalyst and the reusability of the catalyst after several runs without modification. Furthermore, over oxidation of aldehydes to carboxylic acids is not observed by this method. Theoretical calculations on the compounds were carried out at the B3LYP/6-31G level. The geometry optimization, atomic charges, isotropic shielding value (σ_{iso}), thermodynamic parameters, frontier molecular orbitals (FMOs) and molecular electrostatic potentials (MEPs) were discussed.



INTRODUCTION

Oxidation, one the most fundamental reactions in synthetic organic chemistry, has been the subject of numerous studies.^{1,2} Chromium-based reagents play a vital role in organic chemistry as oxidants for alcohols but such transformations are most frequently accomplished by using highly toxic Cr(VI)-based reagents. Chromium-catalyzed oxidations are therefore of particular interest due to concerns of functional group selectivity and environmental factors.³

The oxidation of alcohols to carbonyl compounds is a fundamentally important laboratory and

commercial procedure.⁴⁻⁸ Since the products are valuable both as intermediates and as high value components for the perfumery industry.⁹⁻¹¹

Periodic acid is used as an oxidant in several mild and selective oxidation reactions. Chromium trioxide,¹² pyridiniumchlorochromate,¹³ fluorochromate,¹⁴ bis (trimethylsilyl) chromate,¹⁵ chromium tris (acetylacetonate),¹⁶ Fe(III)/2-picolinic acid¹⁷ and KBr¹⁸ have been used as catalyst for the oxidation of alcohols with periodic acid.

A plethora of reagents are available for this interconversion, but most of these reagents, which are often expensive and toxic, must be used in stoichiometric quantities.

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Scheme 1 – Oxidation of alcohols to aldehydes and ketones with periodic acid catalyzed by S-COCC.

Some of the most applicable, efficient and on the other hand most hazardous reagents used in oxidations are chromium based chemicals. Consequently, from both the environmental and economical points of view catalytic oxidative transformations are thus promising and valuable and those employing less hazardous chromium reagent in catalytic amounts are particularly attractive.

Herein, we report a mild and efficient oxidation of alcohols to the corresponding aldehydes and ketones with periodic acid catalyzed by S-COCC in acetonitrile at room temperature (Scheme 1).

RESULT AND DISCUSSION

To find the optimum reaction conditions, we have chosen the 2-methyl benzylalcohol as a model

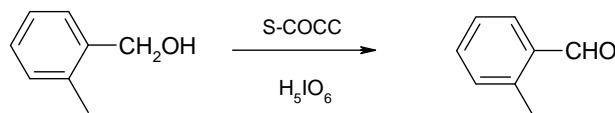
substrate. When we have treated OH compounds with reagent in different solvents, mole ratios of substrate to catalyst and periodic acid at room temperature, we have found the 1: 2: 1 in stirring acetonitril gives the highest yield of the corresponding carbonyl compound (Table 1, entry 1).

To estimate the influence of periodic acid in this research, we performed the reaction of 2-methyl benzylalcohol with catalyst without application any periodic acid. The reaction did not progress after 120 min stirring (Table 1, entry 4).

To show the applicability and generality of this procedure, we have examined the reaction of aromatic and aliphatic alcohols with S-COCC and periodic acid in stirring acetonitril.

Table 1

Effect of periodic acid and S-COCC on the oxidation of model alcohol



| Entry | 1c/mmol | (S-COCC)/mmol | H ₅ IO ₆ /mmol | Time(min) | Yield(%) ^a |
|-------|---------|---------------|--------------------------------------|-----------|-----------------------|
| 1 | 1 | 2 | 1 | 10 | 90 |
| 2 | 1 | 1.5 | 1 | 10 | 88 |
| 3 | 1 | 1 | 1 | 10 | 86 |
| 4 | 1 | 1 | - | 120 | No reaction |
| 5 | 1 | - | 1 | 120 | No reaction |

^a Isolated yield

Table 2

Screening of the solvent on the model reaction

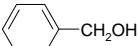
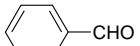
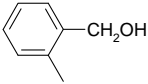
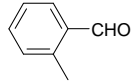
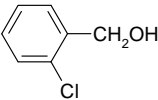
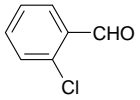
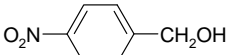
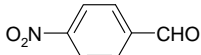
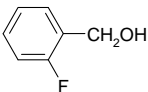
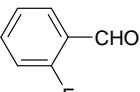
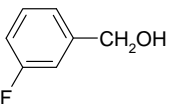
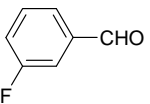
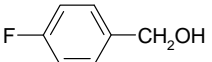
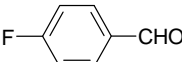
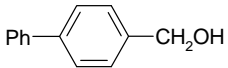
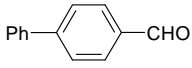
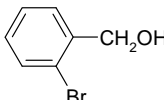
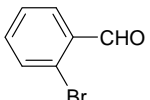
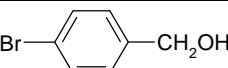
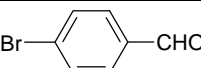
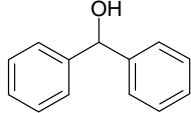
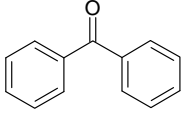
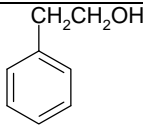
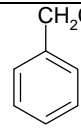
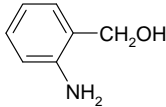
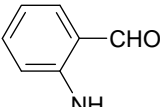
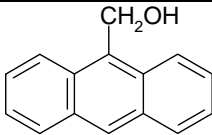
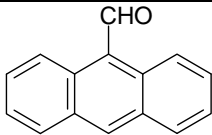
| Entry | Solvent | Time(min) | Yield(%) ^b |
|-------|-----------------------------------|-----------|-----------------------|
| 1 | MeCN | 10 | 100 |
| 2 | CH ₃ COCH ₃ | 120 | 94 |
| 3 | EtOAc | 120 | 83 |
| 4 | n-hexane | 120 | 93 |
| 5 | CH ₂ Cl ₂ | 120 | 90 |
| 6 | CCl ₄ | 120 | 80 |

^a 2-methyl benzylalcohol (1 mmol), S-COCC (2% mmol), H₅IO₆ (1 mmol)

^b Isolated yields

Table 3

Oxidation of alcohols to aldehydes and ketones with periodic acid catalyzed by S-COCC^{a,b}

| Entry | Substrate | Product | Time(min) | Yield(%) ^c |
|-------|---|---|-----------|-----------------------|
| 1 |  |  | 5 | 85 |
| 2 |  |  | 10 | 87 |
| 3 |  |  | 10 | 85 |
| 4 |  |  | 10 | 92 |
| 5 |  |  | 10 | 80 |
| 6 |  |  | 5 | 85 |
| 7 |  |  | 5 | 90 |
| 8 |  |  | 5 | 85 |
| 9 |  |  | 5 | 87 |
| 10 |  |  | 5 | 85 |
| 11 |  |  | 10 | 87 |
| 12 |  |  | 10 | 92 |
| 13 |  |  | 15 | 85 |
| 14 |  |  | 20 | 80 |

^a alcohol (1 mmol), S-COCC (2% mmol), H₅IO₆ (1 mmol), acetonitril, stirring at r.t.^b All the products were identified by comparing IR, NMR, and TLC with those of authentic samples.^c Isolated yields.

The results are tabulated in Table 2. As indicated in this table, varieties of alcohols are

converted to the parent C=O compounds in excellent yield under optimum reactions condition

(Table 3, entries **1-14**). It is considerable that, unlike other oxidation hydrolytic methods, the main burble of overoxidation of the resulting aldehydes is not observed under the reaction conditions. The oxidation efficiency for this catalytic system seems less dependent on the electronic property of substrates. It is interesting to find that the obtained product was carbonyl compound for the substrates with electron-withdrawing groups such as alcohols with electron-donating groups. Interestingly the alcohol **13** underwent to aldehyde **13** very efficiently without, affecting the NH_2 group and the reaction is chemoselective (Table 3, entry 13).

To show the advantage and drawbacks of this method, we have compared some of our results with those reported in the literature. As indicated in the Table 4, this work, compared to the other reagents, performs this transformation in higher

yield, shorter reaction times and milder reaction condition.

Optimized geometry

The optimized geometrical parameters, such as Dipole moment (μ ; Debye), energy of structure formation (HF; kcal/mol) and point group, by B3LYP/6-31G level are listed in Table 5. According to Table 5, geometry of the structures **1-14** is C_1 point group symmetry.

Dipole moment (μ) is a good measure for the asymmetry of a molecule. The values of dipole moment (μ) listed in Table 5 show that largest value of dipole moment obtained for molecule **13**.

According to Table 5, energy of structure formation (HF) for molecules **9** and **10** is more negative, therefore these products are the most stable structure and product **1** is more unstable structure.

Table 4

Oxidation of benzylalcohol by S-COCC in comparison with other catalysts

| Entry | Catalyst | Condition(°C) | Time(min) | Yield(%) ^a | References |
|-------|---|---------------|-----------|-----------------------|------------|
| 1 | S-COCC | r.t | 5 | 95 | This work |
| 2 | [Ru(acac) ₂ (CH ₃ CN) ₂]PF ₆ | r.t | 60 | 91 | [4] |
| 3 | PCC | 0-r.t | 120 | 72 | [13] |
| 4 | PFC | 0 | 120 | 67 | [14] |
| 5 | BTSC | 40-50 | 60 | 96 | [15] |
| 6 | Cr(acac) ₃ | r.t | 180 | 93 | [16] |
| 7 | Fe(III)/PA | r.t | 240 | 74 | [17] |

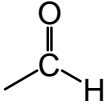
^a Isolated yields

Table 5

Dipole moment (μ), HF and point group of molecules **1-14** obtained using B3LYP/6-31G level

| | HF (kcal/mol) | μ (Debye) | Point group |
|----|------------------|------------------|----------------|
| 1 | -216794.954 | 3.666 | C_1 |
| 2 | -241459.684 | 3.723 | C_1 |
| 3 | -505180.356 | 3.761 | C_1 |
| 4 | -345067.421 | 2.875 | C_1 |
| 5 | -279051.117 | 3.856 | C_1 |
| 6 | -279051.233 | 2.001 | C_1 |
| 7 | -279052.029 | 2.243 | C_1 |
| 8 | -361753.697 | 4.276 | C_1 |
| 9 | -1830103.131 | 3.673 | C_1 |
| 10 | -1830103.725 | 2.298 | C_1 |
| 11 | -361755.160 | 3.316 | C_1 |
| 12 | -241453.079 | 3.050 | C_1 |
| 13 | -251520.654 | 4.751 | C_1 |
| 14 | -409568.010 | 4.002 | C_1 |

Table 6
Atomic charge and isotropic shielding values of C, O and H (aldehyde group)
of structures **1-14** obtained using B3LYP/6-31G level

|  | C | | O | | H | |
|---|---------------|-----------------------------|---------------|-----------------------------|---------------|-----------------------------|
| | Atomic charge | σ_{iso} (ppm) | Atomic charge | σ_{iso} (ppm) | Atomic charge | σ_{iso} (ppm) |
| 1 | 0.156 | 1.766 | -0.396 | -359.797 | 0.111 | 22.011 |
| 2 | 0.156 | 3.572 | -0.399 | -362.565 | 0.111 | 21.467 |
| 3 | 0.164 | 3.584 | -0.389 | -357.903 | 0.149 | 21.666 |
| 4 | 0.165 | 1.465 | -0.375 | -400.741 | 0.126 | 21.928 |
| 5 | 0.171 | 5.935 | -0.394 | -371.270 | 0.143 | 21.515 |
| 6 | 0.163 | 2.475 | -0.388 | -370.420 | 0.118 | 22.036 |
| 7 | 0.157 | 3.686 | -0.394 | -358.597 | 0.114 | 22.083 |
| 8 | 0.154 | 2.492 | -0.399 | -357.467 | 0.109 | 22.016 |
| 9 | 0.159 | 2.043 | -0.391 | -373.178 | 0.141 | 21.738 |
| 10 | 0.160 | 2.853 | -0.391 | -364.225 | 0.115 | 22.099 |
| 11 | 0.187 | -4.592 | -0.421 | -337.824 | - | - |
| 12 | 0.240 | -6.414 | -0.382 | -396.196 | 0.120 | 22.116 |
| 13 | 0.151 | 12.646 | -0.409 | -316.841 | 0.082 | 21.845 |
| 14 | 0.159 | 2.879 | -0.412 | -360.177 | 0.115 | 20.325 |

In Table 6, C atom (carbonyl group) of structure **12** has the highest positive atomic charge (0.240 e), therefore this atom can be suitable places for nucleophilic attack. Also this atom has the smallest isotropic shielding value (σ_{iso}), which is -6.414, therefore it is more influenced by the magnetic field. The C atom of structure **13** has lowest positive atomic charge. The O atom of structure **4** has the lowest negative atomic charge which is -0.375 and smallest value isotropic shielding value (σ_{iso}), which is -400.741. In structure **3**, H atom of aldehyde has highest positive atomic charge which is 0.149 and the smallest value isotropic shielding value (σ_{iso}) is watched for H atom of structure **14** which is 20.325.

Frequency calculations

Thermodynamic parameters such as the relative energy (ΔE), standard enthalpies (ΔH), entropies (ΔS), Gibbs free energy (ΔG) and constant volume molar heat capacity (C_v) values of structures **1-14** were obtained by theoretical methods using B3LYP/6-31G level. The results listed in Table 7 show that relative energy, Gibbs free energy and standard enthalpies values of all structure are negative, therefore we found all structure are stable. As pointed in Table 7, we found that structures **9** and **10** have the highest negative value, therefore are more stable, while structure **1** has the lowest negative value. Also the largest

values of entropies (ΔS) and C_v were observed for structure **14**.

Frontier molecular orbital analysis

The E_{HOMO} , E_{LUMO} and HOMO-LUMO energy gap (ΔE) of molecules **1-14** were calculated using the B3LYP/6-31G level. The properties of molecular orbitals such as energy and frontier electron density are important and are used to determine the reactive position.

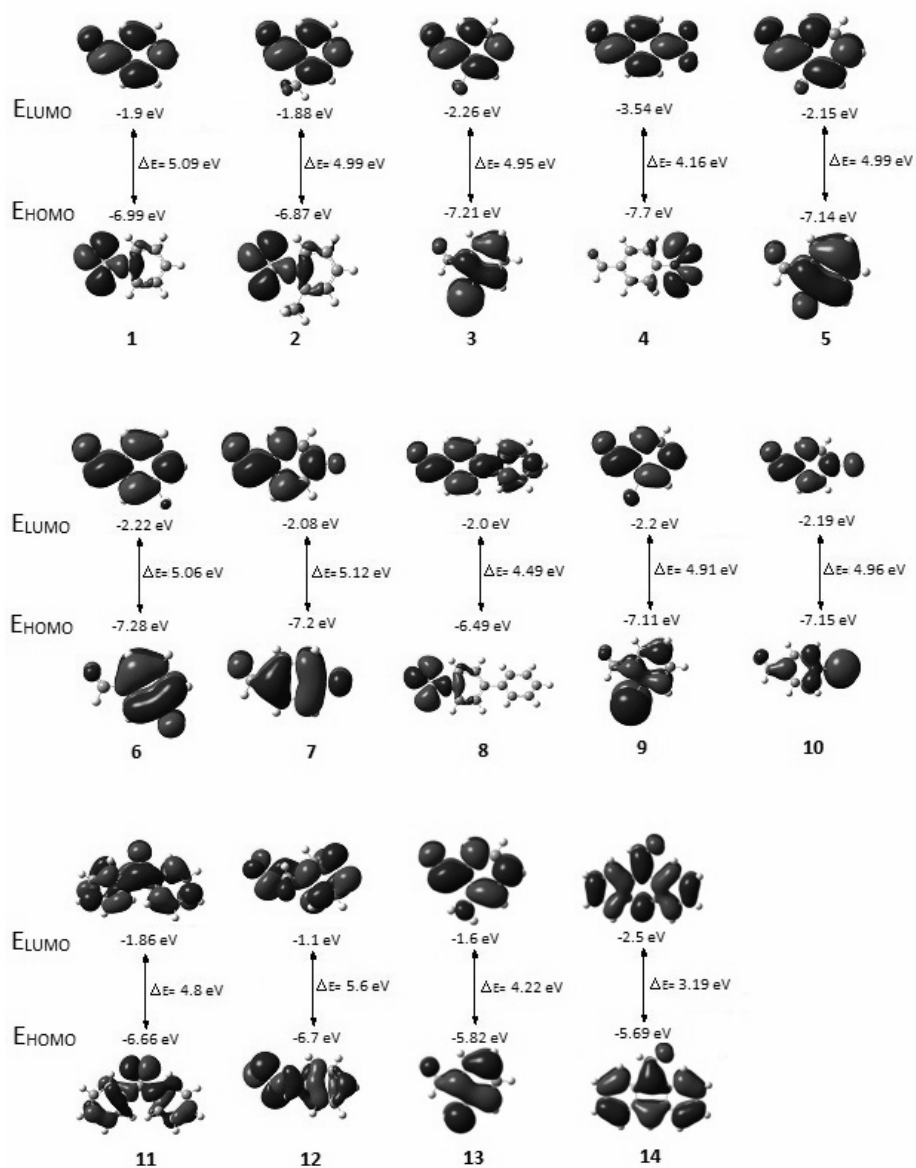
A large energy gap implies high stability for the molecule.^{19,20} Fig.1 and spectrum DOS (Fig. 2) show that energy gap of structure **12** is the highest value (5.6 eV) therefore it is the more stable structure and less reactive than other structure. Also energy gap of structure **13** is the lowest value (4.16 eV), which indicates it is most unstable.

The HOMO can act as an electron donor and the LUMO can act as the electron acceptor.¹⁹ A higher HOMO energy (E_{HOMO}) of the molecule indicates a higher electron-donating ability to an appropriate acceptor molecule with a low-energy empty molecular orbita.²¹ The LUMO energy (E_{LUMO}) indicates the ability of the molecule to accept electrons; the lower the value of E_{LUMO} , the more probable it is that the molecule will accept electrons. As shown in Fig. 1, structures **3**, **5**, **6**, **7**, **9**, **10** which have halogen atom, the HOMO is focused mainly around aromatic system and halogen atom, While LUMO orbital is focused mainly on carbonyl group and extent benzene ring.

Table 7

The Calculated thermodynamic parameters of molecules 1-14 using B3LYP/ 6-31G level

| | E(Kcal/mol) Δ | ΔG (Kcal/mol) | ΔH (Kcal/mol) | S(cal/molK) | C_V (cal/molK) |
|----|----------------------|-----------------------|-----------------------|-------------|------------------|
| 1 | -216721.299 | -216744.284 | -216720.706 | 79.078 | 23.369 |
| 2 | -241367.384 | -241392.614 | -241366.792 | 86.609 | 29.283 |
| 3 | -505112.044 | -505137.203 | -505111.452 | 86.369 | 27.377 |
| 4 | -344991.190 | -345018.476 | -344990.597 | 93.507 | 32.231 |
| 5 | -278982.147 | -279006.464 | -278981.555 | 83.546 | 26.464 |
| 6 | -278982.415 | -279006.777 | -278981.823 | 83.697 | 26.532 |
| 7 | -278983.162 | -279007.495 | -278982.569 | 83.602 | 26.464 |
| 8 | -361625.745 | -361655.872 | -361625.152 | 103.037 | 42.142 |
| 9 | -1830034.796 | -1830060.585 | -1830034.204 | 88.480 | 27.494 |
| 10 | -1830035.504 | -1830061.456 | -1830034.911 | 89.031 | 27.532 |
| 11 | -361626.859 | -361656.894 | -361626.266 | 102.725 | 41.648 |
| 12 | -241360.868 | -241387.216 | -241360.275 | 90.360 | 28.490 |
| 13 | -251435.479 | -251460.457 | -251434.886 | 85.765 | 29.512 |
| 14 | -409431.526 | -409462.777 | -409430.933 | 106.807 | 46.511 |

Fig. 1 – Frontier molecular orbitals of structures 1-14. (ΔE : Energy Gap between LUMO and HOMO).

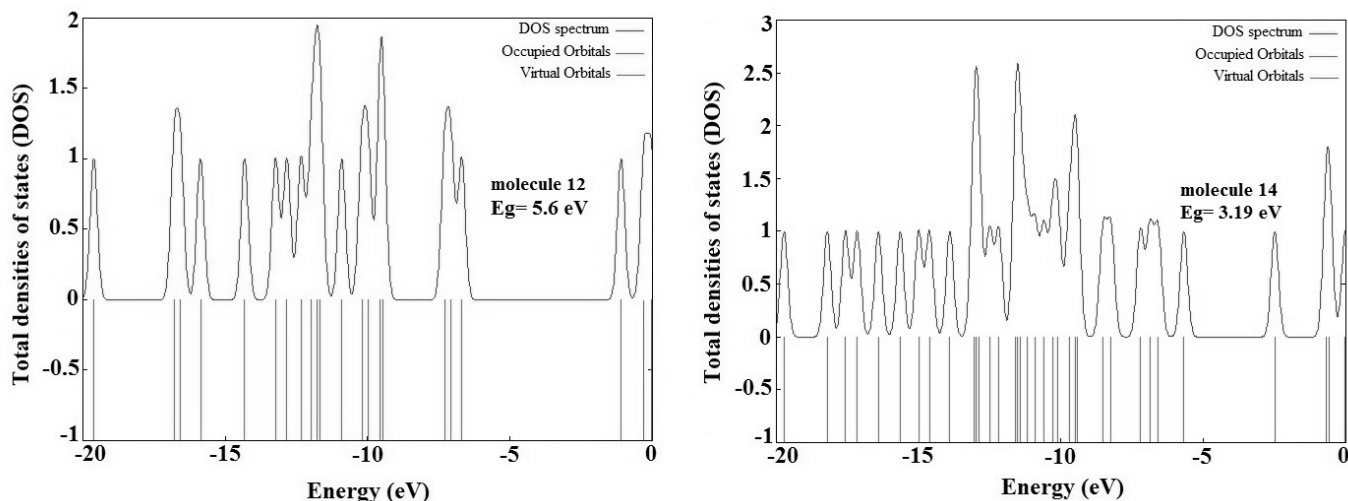


Fig. 2 – Total densities of states (DOSs) for structures 12 and 14.

Molecular Electrostatic Potential

Molecular electrostatic potential (MEP) is the physical property that explores the electronic density and the polarization. MEP parameter can be used to indicate the electrophilic and nucleophilic sites in the molecules where chemical reactions are expected to occur.^{22,23} Fig. 3 shows the theoretical MEP obtained from B3LYP/6-31G level, with the electronegative and electropositive

regions of the structures 1-14. According to Fig. 3, negative center include oxygen atom of carbonyl group.

The structure 4 has the lowest electronic density at around oxygen of carbonyl due to the presence of the nitro electron-drawing group on the aromatic ring, while structure 13 has the highest electronic density at around oxygen of carbonyl that there is amino group (NH₂) on aromatic ring.

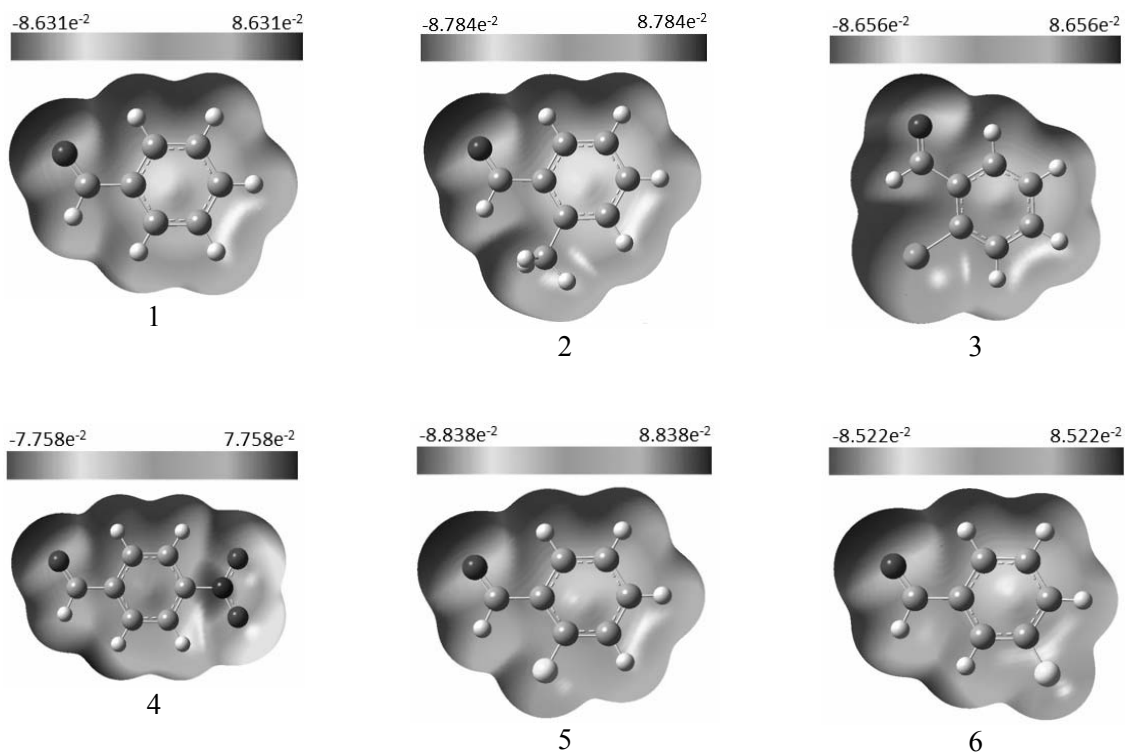


Fig. 3 – The Molecular electrostatic potential surface of structures 1-14.

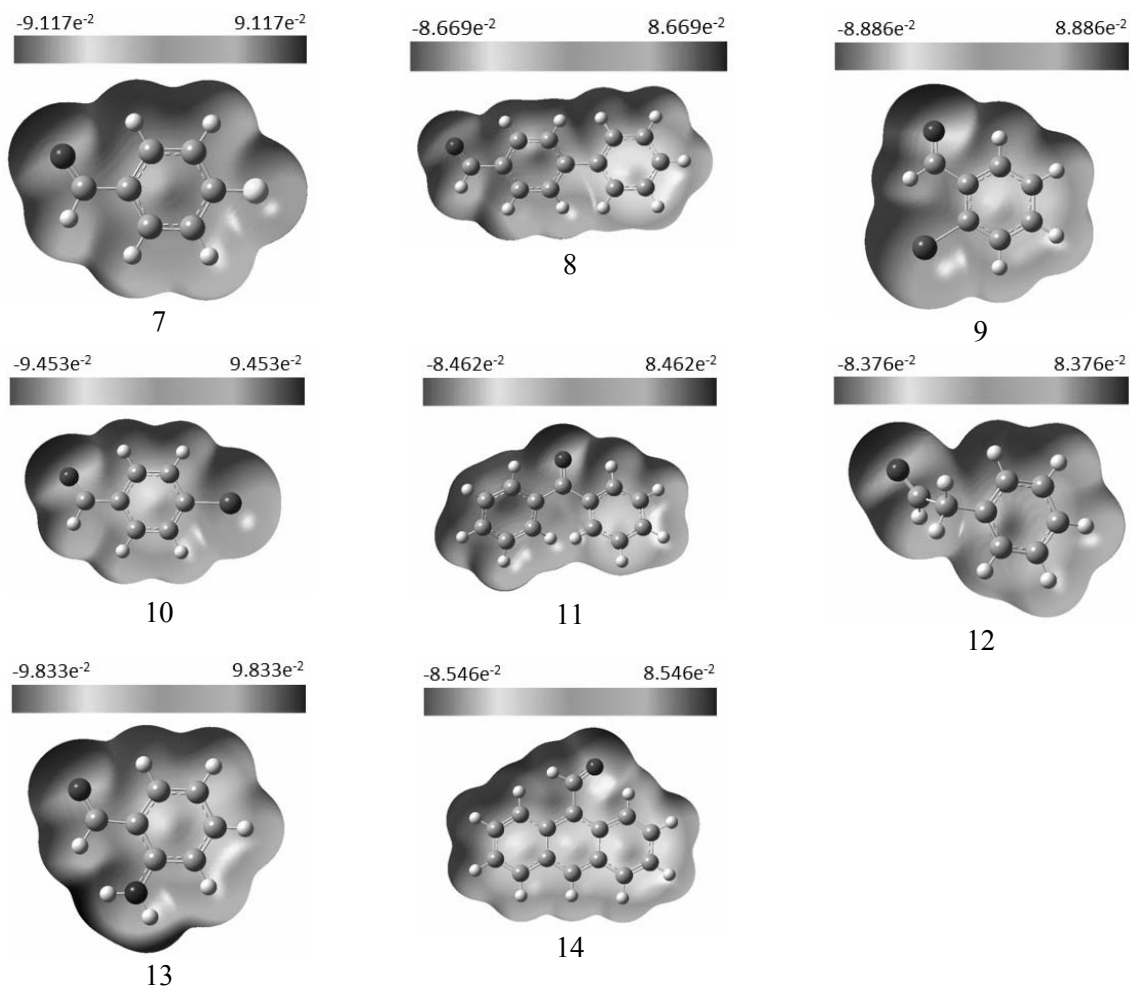


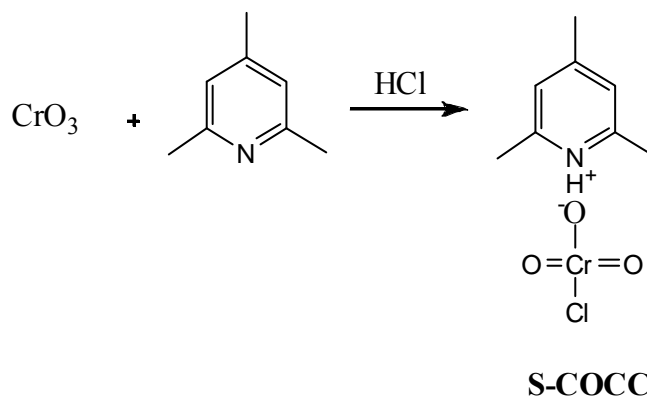
Fig. 3 (continued) – The Molecular electrostatic potential surface of structures **1-14**.

EXPERIMENTAL

Materials used in this article were prepared from Fluka and Merck companies and reagents were used without extra purification, but solvents were purified with standard methods. All compounds were known and identified by comparison of

their physical and spectroscopic data with those of authentic samples. Melting points were measured on a SMPI apparatus. The solvent was evaporated by Rotavapor IKA R-300.

Common approach for the Synthesis of Sym-Collidinium Chlorochromate (S-COCC)²⁴



Scheme 2 – Schematic representation of preparation process for S-COCC.

Typical procedure for the oxidation alcohols to aldehydes and ketones using periodic acid catalyzed by S-COCC

A solution of acetonitril (10 mL, 1mmol) and periodic acid was placed in flask and stir for the 15 min. Then, a mixture of alcohols (1mmol) and S-COCC (1%mmol) was added and the resulting mixture was stirred at room temperature for a suitable period (Table 3) and completion of the reaction investigated by TLC (*n*-hexane/EtOAc; 2:1) analysis. Then, EtOAc (20ml) was subjoined to the reaction mixture and after being washed with water/sodium sulfite(1:1), the mixture was filtered off. The solvent was vaporized and produced pure products.

METHODS OF COMPUTATION

Theoretical calculations were employed by DFT method using B3LYP level and 6-31G basis set by the Gaussian 03 program.²⁵ The properties such as Hartree-Fock energy (HF), dipole moment (μ), Point group, atomic charges, isotropic shielding value (σ_{iso}), thermodynamic parameters. The HOMO and LUMO orbitals energy levels (EHOMO, ELUMO), energy gap (ΔE) between LUMO and HOMO and spectrum densities of state (DOS) obtained. We were visualized HOMO and LUMO surfaces using GaussView 03 program.²⁶ Also the thermodynamic calculations were performed and obtained the energy (ΔE), enthalpies (ΔH), Gibbs free energy (ΔG), entropies (S) and constant volume molar heat capacity (Cv) of compound.²⁷

CONCLUSIONS

All in all, we have reported a novel and effective system for the regeneration of carbonyl compounds from alcohols. The durability and facile preparation of S-COCC, easy workup way, high yields of the products and low reaction time, make this method a novel and useful one relative to the reported method for regeneration of Aldehydes and ketones from their derivatives. These features make S-COCC a mild and efficient catalyst for oxidation of alcohols to aldehydes and ketones. Then, we performed theoretical calculations using B3LYP/6-31G level. The molecular properties such as atomic charges, isotropic shielding value, Dipole moment (μ), energy of structure formation (HF) and point group were calculated, thermodynamic parameters, frontier molecular orbitals (HOMO and LUMO), electronic density (MEP) were obtained. The thermodynamic parameters we found that all molecules are stable. According to Frontier Molecular Orbital (FMO) analysis energy gap of structure **12** is the highest value (5.6 eV)

therefore it is the most stable structure and energy gap of structure **14** is the lowest value (4.16 eV), which indicates it is the most unstable. The MEP parameter showed that negative center includes oxygen atom of carbonyl group. The structure **4** has the lowest electronic density at around oxygen of carbonyl due to the presence of the nitro (NO₂) and structure **13** has highest electronic density at around oxygen of carbonyl due to the presence of amino group (NH₂).

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