Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2013, 2 (1): 42-49

(International Peer Reviewed Journal)

Simulation Study of Oxidation for Oleic acid by $KMnO_4$ Using Theoretical Calculations

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Received on 07th January and finalized on 17th January 2013

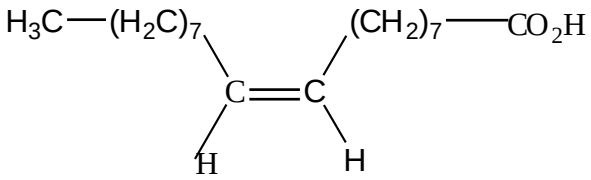
ABSTRACT

Simulation study of oxidation for Oleic acid has been carried out using semi-empirical methods (PM3 and AM1) that are packaged on hyperchem 8.0.9 program. Geometrical properties and vibration spectrums have been calculated. Five different transition states have been suggested and the most probable transition state been investigated depending upon the electronic properties to suggest the most probable pathway of the reaction. The calculations show that first transition state is the most probable than other state due its energetic values of total energy, binding energy, heat of formation, zero pointenergy, and imaginary frequency that's equal to -111016.403, -5670.849, -398.307, 314.119 respectively by kCal mol^{-1} units .The pathway of reaction is spontaneous and exothermic with the change in Gibes energy value and heat of formation value equal to -36122.691 and -110745 respectively

Keywords: semiempirical calculations, transition state, Oleic acid, Dihydroxy stearic acid, oxidation, $KMnO_4$.

INTRODUCTION

Oleic acid is one members of fatty acid, since its unsaturated with normal chain and mono carboxyl group. Acid has low melting point equal to (13C°) and eighteenth carbon atom. Oleic acid has one double bond in (9) position with two isomers , cis or Z-isomer[1-3] because the groups on either end of the double bond at the same direction in the space so it's systematic name is (z)-9-octa decenoic acid[4-5].



Oleic acid which used as anti-Breast cancer, can be obtained from olive oil which contain 84% oleic acid with 4% linoleum acid and only 11% saturated fatty acid as components [6].oxidation of double bond is one of the most important reactions in organic chemistry [1].Recent research shows that oxidation of double bond can be achieved by using different oxidizing agents [7-13]. In the present work, semiempirical calculation will be done to simulate the reaction of synthesis. The oxidization process will done on the oleic acid using $KMnO_4$ to get 9,10-dihydroxy stearic acid(DHSA) ,Five different transition

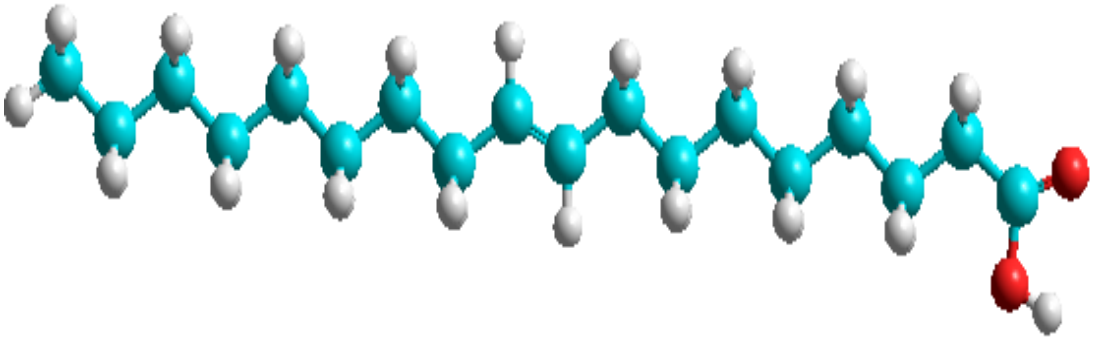
states are suggested to find the most probable transition state which can be occur to give up the final product.

MATERIALS AND METHODS

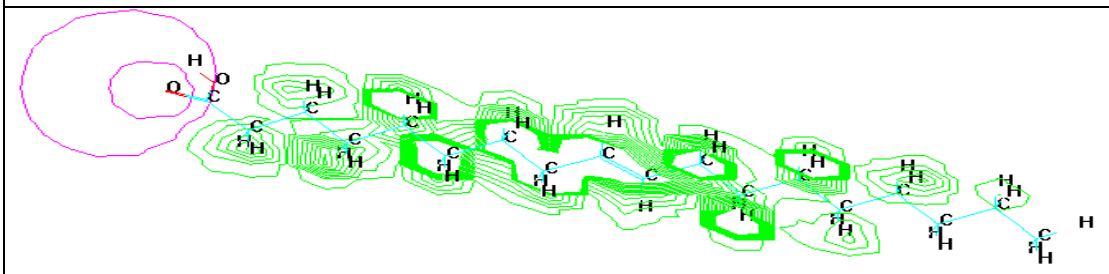
Geometry optimization, electronic energies, heat of formation and electrostatic potential energy of oleic acid and D.H.S.A. were performed by theoretical calculations of semi-empirical method, AM1 and PM3 level, by using the hyper chem. Version 8.0.9 program [14, 15]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are performed [16]. Energy gap (ΔE), bond lengths and the charge of atoms [17]. Thermodynamic parameters (ΔG, ΔH, ΔS) have been estimated at semi-empirical method, AM1 and PM3 level,by using the hyper chem. Version 8.0.9 program [18].

RESULTS AND DISCUSSION

Energetic properties of Oleic acid were calculated using geometry optimization, semi-empirical method (PM3 and AM1) as shown in figure1.



Atomic Ball view



Electrostatic potential in two dimension.

Figure1. Geometry optimization of Oleic acid calculated by semiempirical method**.**

Oxidation of oleic acid with $KMnO_4$ can undergo in several steps to produce some probable products. D.H.S.A is the most probable product because it have the lowest total energy, binding energy, and heat of formation that's equal to -89169.288, -5454.722, -264.794 respectively through PM3 and equal to -94256.112, -5486.390, -296.462 respectively through AM1 .Table1 shows the energetic properties for all the probable products.

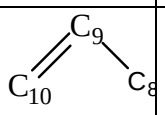
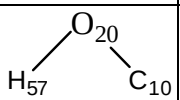
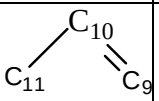
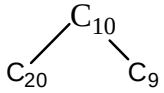
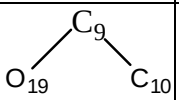
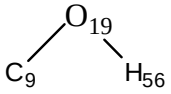
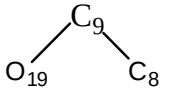
Table1. Energetic properties for the probable products of oxidation process to the oleic acid using $KMnO_4$ by semiempirical calculations.

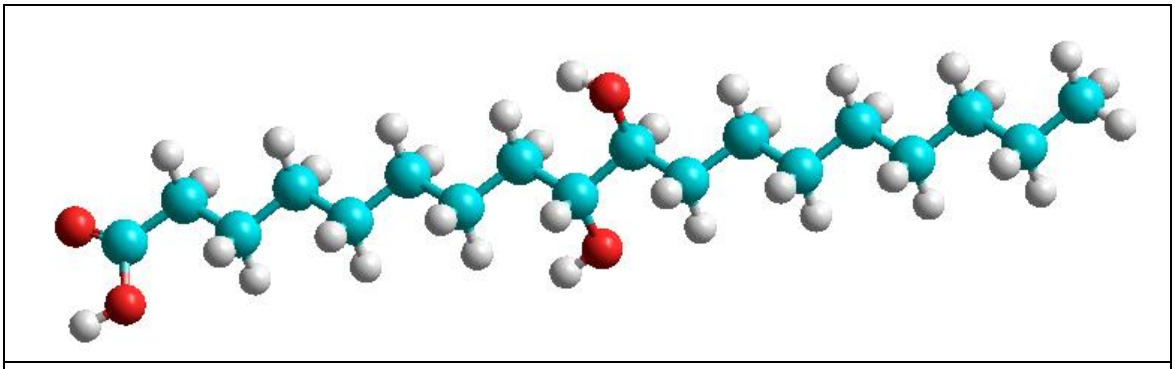
substance	Total Energy		Binding Energy		Heat of Formation	
	AM1	PM3	AM1	PM3	AM1	PM3
Oleic acid	-78814.562	-74893.712	-5149.611	-5127.130	-183.005	-160.524
nonal	-39720.377	-37802.167	-2625.098	-2617.400	-89.693	-81.995
D.H.S.A	-94256.112	-89169.288	-5486.390	-5454.722	-296.462	-264.794
9-al-n.a	-53872.959	-50640.778	-2724.122	-2713.932	-173.803	-163.613
Nonoic acid	-47129.822	-44590.515	-2744.961	-2733.232	-149.997	-138.268
N.D.O.A Nonane dioic acid	-61282.415	-57429.105	-2843.996	-2829.743	-234.118	-219.865

The calculus of energy in kCal mol^{-1} units.

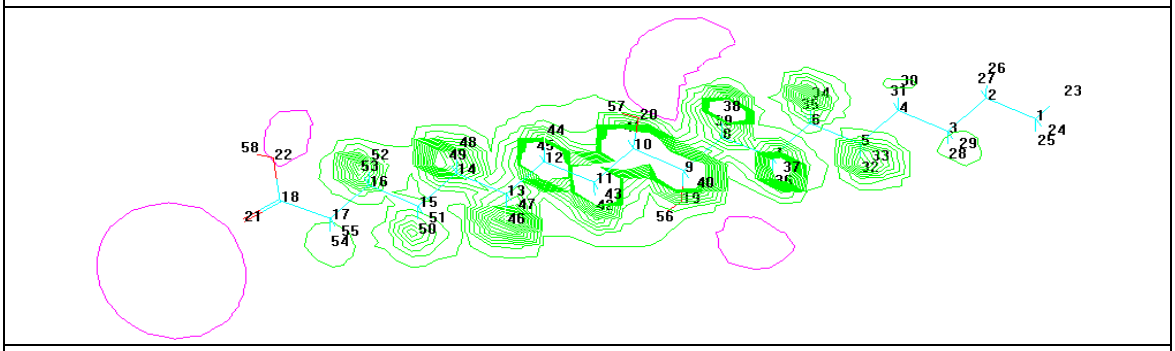
The calculated values of bond length (Å) and bond angle may be closer to practical value [18]. Bond angle of Oleic acid on the both sides of the double bond are so that the reaction can occur on any side of the double bond of oleic molecule as shown in the calculation of table 2. The physical properties of D.H.S.A. represented in Figure 2. The negative electrostatic potential regions are differ in some atoms therefore there are incomplete distribution of electrostatic potential on the atoms and also in total charge.

Table 2 . Semiempirical calculation of Bond lengths and bond angle for Oleic acid and D.H.S.A. molecule.

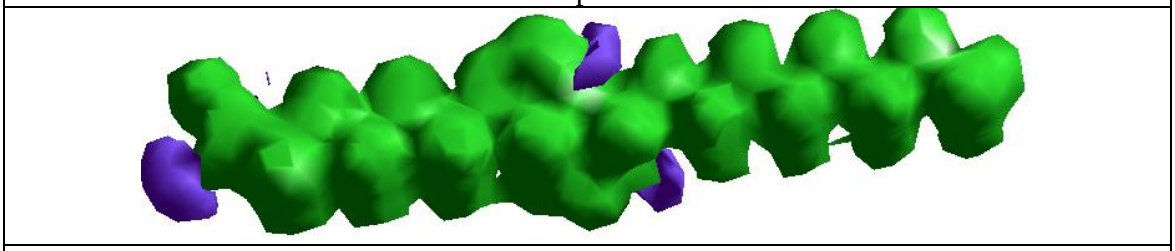
Oleic acid				9,1-Dihydroxy stearic acid			
Bond	Bond length A°	Bond	Bond angle(°)	Bond	Bond length A°	Bond	Bond angle(°)
C_8—C_9	1.482		122.96	C_9—C_{10}	1.560		105.715
C_{10}—C_{11}	1.482		122.87	C_9—O_{19}	1.416		107.195
C_9=C_{10}	1.336			C_{10}—O_{20}	1.415		110.889
				O_{19}—H_{56}	0.951		106.630
				O_{20}—H_{57}	0.952		106.592



Atomic Ball view



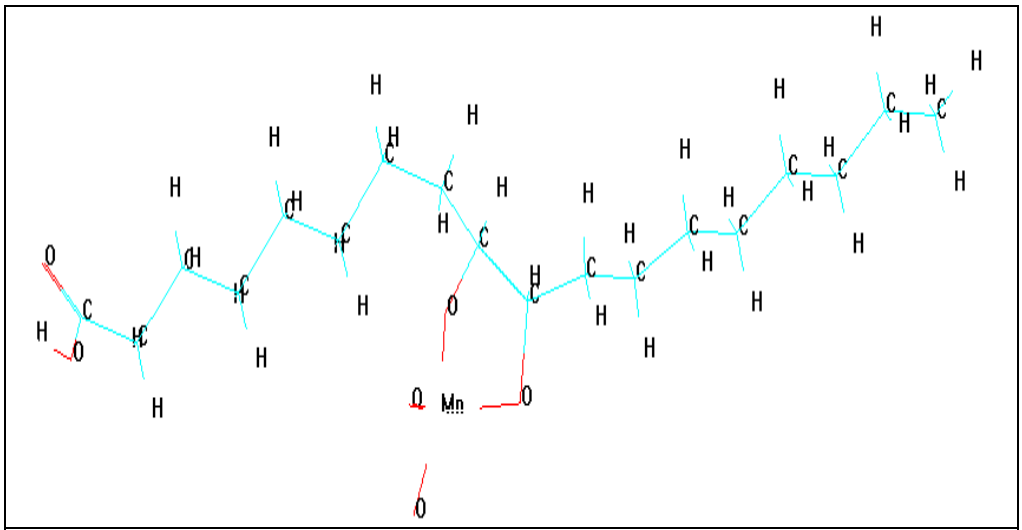
Electrostatic potential at 2D



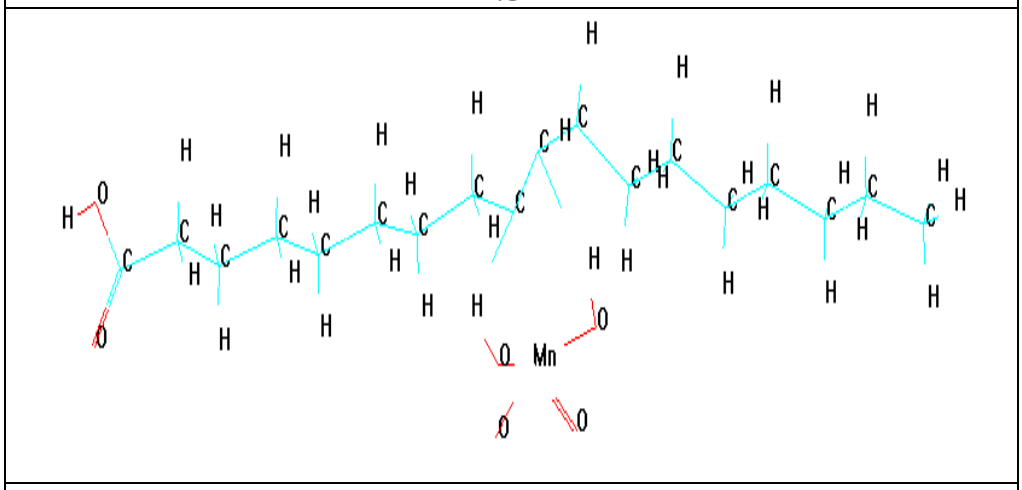
Electrostatic potential at 3D

Figure 2. Geometry optimization of 9, 10-Dihydroxy stearic acid calculated at PM_3.

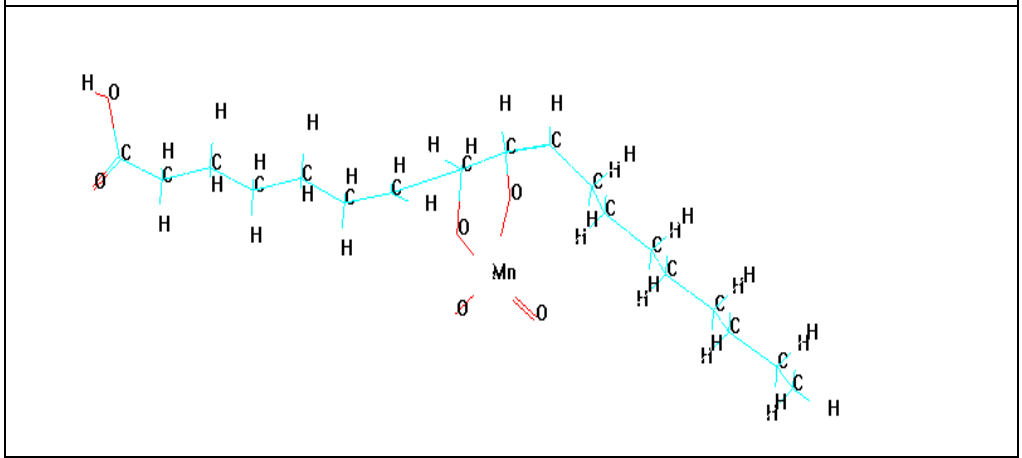
Different five transition states of oxidation reaction have been suggested that's have been examined to estimate the most probable transition state to give up the product as shown in Figure 3.



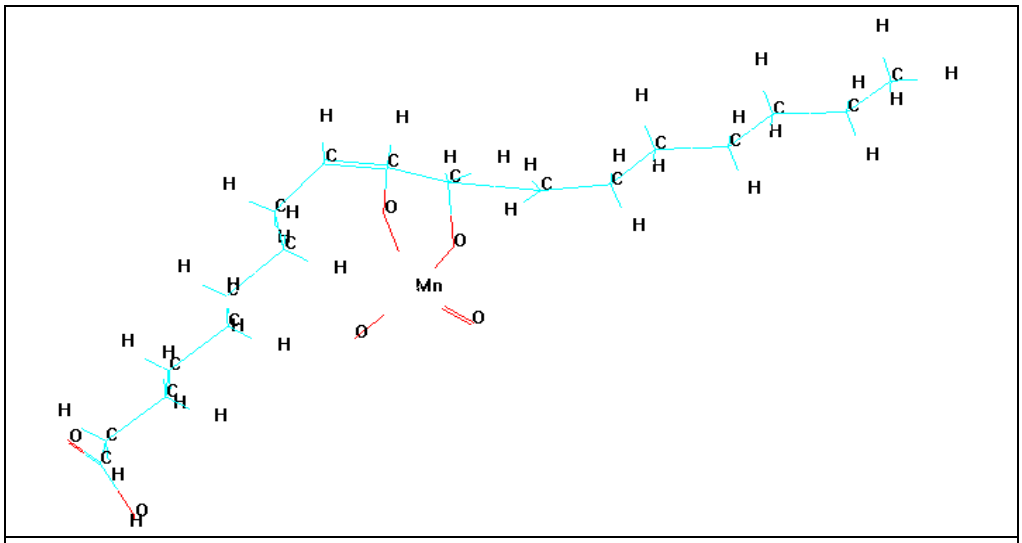
T.S-1



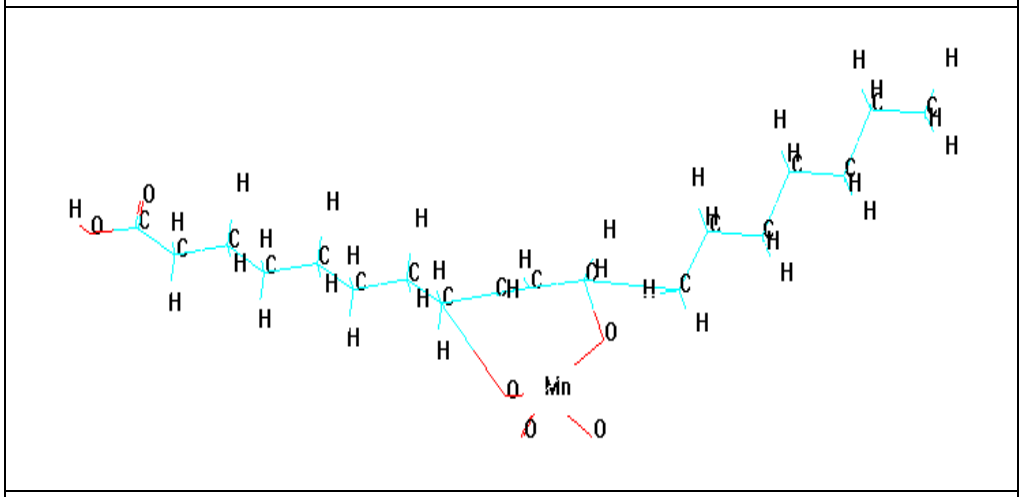
T.S-2



T.S-3



T.S-4



T.S-5

Figure 3. The geometrical structures of suggested transition state for oxidation reaction calculated by semiempirical method.

According to structural properties like First imaginary frequency and zero point energy, all transition states are unstable except T.S-2 so it can't act as transition state. Electronic properties shows that the most probable transition state is T.S-1 in which $KMnO_4$ molecule joined to double bond of oleic acid to give (D.H.S.A) as product , which is exothermic and spontaneous reaction with ΔH and ΔG equal to -36122.691 and -110745 respectively with energy gap equal to 2.0291 kCal mol^{-1} .Also the lowest energy barrier value related to T.S-1 as shown in Table 3.

Table 3 . Electronic properties and Z.P.E. of the probable transition states.

Energy calculation	T.S-1	T.S-2	T.S-3	T.S-4	T.S-5
Total Energy (kCal mol^{-1})	-111016.403	-110986.750	-110986.124	-110986.750	-110933.180
Binding Energy (kCal mol^{-1})	-5670.849	-5641.196	-5640.570	-5641.196	-5587.627
Energy gap (kCal mol^{-1})	-398.307	-368.654	-368.028	-368.654	-315.085
Z.P.E.(kCal mol^{-1})	314.119	310.196	310.037	310.196	309.298
1^{st}- imaginary frequency	-	+	-	-	-
Energy barrier (kCal mol^{-1})	14871.047	14900.700	14901.326	14900.700	14954.270
HOMO(ev)	0.6288	0.7173	-0.7318	-0.7254	-0.2585
LUMO(ev)	2.6579	2.6467	2.3090	2.2903	2.1560
ΔE (kCal mol^{-1})	2.0291	1.9294	3.0408	3.0157	2.4145
ΔS(kCal mol^{-1} deg^{-1})	0.2054	0.2146	0.2146	0.2187	0.2273
ΔG(kCal mol^{-1})	-110745	-110726	-110721	-110718	-110705
ΔH(kCal mol^{-1})	-36122.691	-36093.038	185879.836	-36093.038	-36039.468

The distance of bonds Mn_{57}—O_{55} and Mn_{57}—O_{56} are 1.839 and 1.890 respectively but the bond angle of C_{10}-O_{55}-Mn_{57} and C9-O_{56}-Mn_{57} are 98.836 and 101.146 respectively so the ring can broken first from Mn_{57}—O_{55} bond to give the product as shown in Table4.

Table 4 . Bond lengths (Å) and bond angle of T.S-1 molecule

Bond	Bond length A°	Bond	Bond angle(°)
Mn_{57}—O_{56}	1.890	O_{58}=Mn_{59}-O_{59}	99.644
Mn_{57}—O_{55}	1.893	O_{58}=Mn_{59}-O_{56}	112.063
Mn_{57}—O_{59}	1.637	O_{58}=Mn_{59}-O_{55}	127.451
Mn_{57}=O_{58}	1.667	O_{55}-Mn_{59}-O_{59}	117.344
C_9—O_{56}	1.422	O_{55}-Mn_{59}-O_{56}	84.696
C_{10}—O_{55}	1.407	C_9-O_{56}-Mn_{57}	101.146
C_9=C_{10}	1.580	C_{10}-O_{55}-Mn_{57}	98.836
C_8—C_9	1.538	O_{565}-C_{10}=C_9	109.092
C_{10}—C_{11}	1.543	O_{56}-C_9=C_{10}	110.491

APPLICATION

The method is useful in finding most probable transition state in the reaction.

CONCLUSIONS

Dihydroxy stearic acid is the most probable product in the oxidation reaction of oleic acid by $KMnO_4$ according to energetic properties. The reaction follow first suggested pathway which is exothermic and spontaneous reaction with ΔH and ΔG equal to -36122.691 and -110745 respectively and energy gap equal to 2.0291 kCal mol^{-1}.

REFERENCES

[1] B.James , Hendrickson, J. Donald , Cram and S..George, Hammond, Organic Chemistry, 3rd Ed., 1970. .

[2] A.Franscis Carey, Organic Chemistry, 6th Ed., New York, University of Virginia, 2006.

[3] Bhupinder Mchta and Manju Mehta,Organic Chemistry,4th Ed. ,New Delhi,**2009**.

[4] G. Marc Loudon, Organic Chemistry, 4thEd. , New York, oxford University Press, **2002.**

[5] Abbas A-Ali Drea, *J. Nation. Chem*, **2010**, **(**37**)**, 86-100.

[6] Janice Gorzynski Smith,Organic Chemistry,1st Ed. , New York, University of Hawai i at Ma noa,**2006**.

[7] Aqeel A-Hussein, and Abbas A-Ali Drea, *Journal of Applicable Chemistry*, **2012**, 1 (3):453-459.

[8] Jhillus. Yadav, Basi V.subba Reddy, Ashutosh P.Singh and Ashok K.Basak, *Tetrahedron Letters*, **2008**, 49.

[9] Robert Thornton Morrison and Robert Neilson Boyd,"Orgonic Chemistry", 6th Ed. , New York University,**2002**.

[10] Sukalyan Dash, Sabita Patel and Bijay K.Mishra, *Tetrahedron*, **2009**, 65.

[11] Fangwei Liu,Reema Anis, Eunmi Hwang, Rafael Ovalle, Armando Varela-Ramirez,Renato J.Aguilera and Maria Contel, molecules,16,**2011**.

[12] Thanapat Sastraruji, Staphen G.Pyne and Alison T.Ung, *Tetrahedron*, **2012**, 68.

[13] Fadhel Omran Essa, Kadhum Jwad Kadhum, and Abbas A-Ali Drea, *Journal of Applicable Chemistry*, **2012**, 1 (3):344-351.

[14] Abbas.A-Ali Drea, Salah A.Naman and Bhjat R.Jaffer, *Journal of Applicable Chemistry*, **2012**, 1 (1): 125-136.

[15] Mohamed H. Obies, Abbas A-Ali Drea and Falah H. Hussein, *Int. J. Chem. Sci.:* **2012**, 10(1), 63-79.

[16] Abbas A- Ali Drea and Nadia Izet. *Journal of photocatalysis science*, **2012,** 3(2), 49-59.

[17] Aqeel A-Hussein and Abbas A-Ali Drea, *Journal of Applicable Chemistry*, **2012**. 1(2), 319-329.

[18] G.Marc Loudon,Organic Chemistry, 4th Ed.,Oxford University Press,Inc,**2002.**